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**THERMALLY STABLE AROMATIC STRUCTURES FROM ACYCLIC
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AERONAUTICAL LABS WRIGHT-PATTERSON AFB OH.**


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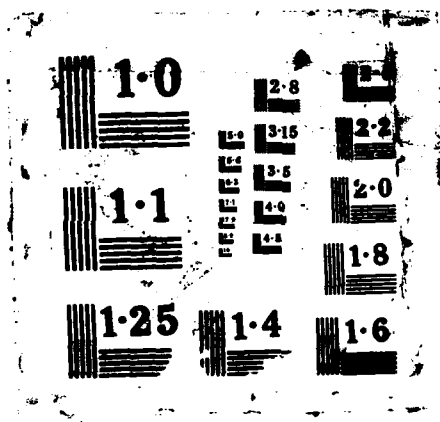
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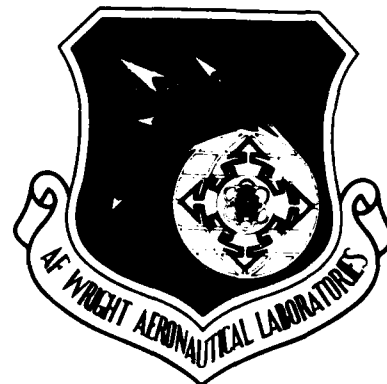
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THERMALLY STABLE AROMATIC STRUCTURES FROM ACYCLIC
PRECURSORS I: para-POLYPHENYLENE MODEL COMPOUNDS
FROM 3-DIMETHYLAMINOHEX-5-EN-1-YNES



Marilyn R. Unroe and Bruce A. Reinhardt
Polymer Branch
Nonmetallic Materials Division

July 1987

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			Stevens rearrangement thermally stable ammonium bromides		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Condensation of N,N-dimethyl-(3phenylprop-2-ynyl) amines with cinnamyl bromides of various structure afford cinnamyldimethyl-(3-phenylprop-2-vnyl) ammonium bromides in high yield. Without isolation, the ammonium salts can undergo both [3,2] and [1,2]base catalyzed Stevens rearrangements to the corresponding 3-dimethylamino-1,4-diphenylhex-5-en-1-ynes. Subsequent heating of the rearranged products closes the [3,2] linkages preferentially forming the all <u>para</u> -polyphenyls which are isolated easily from the reaction mixtures.					
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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. I. J. Goldfarb as the Materials Laboratory Project Scientist. Co-authors were Marilyn R. Unroe and Bruce A. Reinhardt, Materials Laboratory (AFWAL/MLBP).

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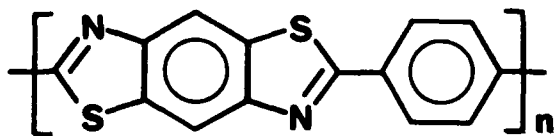
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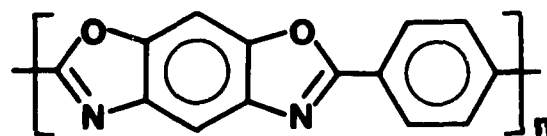
SECTION I

INTRODUCTION

As part of a continuing Air Force research effort directed toward the development of new high performance structural materials, a substantial amount of work has involved the synthesis and characterization of various totally aromatic rigid-rod polymers (Reference 1). Representative examples of this class of all para rodlike molecules are poly (p-phenylenebenzobisthiazole) (PBT) and poly (p-phenylenebenzobisoxazole) (PBO).

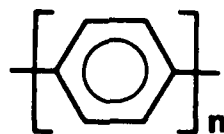


PBT



PBO

The intractable poly (p-phenylene) is another member of this class of



poly(p-phenylene)

materials which has thus far received little attention in this laboratory. Poly (p-phenylene) has been studied extensively the past 25 years (Reference 2) because of its excellent thermal stability. These materials, however, have had rather limited applications because their extreme insolubility and exceptionally high melting points make fabrication extremely difficult. Generally the materials previously prepared were of low or indeterminate molecular weight and in some cases were contaminated with metal impurities.

It was postulated that a new synthetic method which generated the p-polyphenylene linkage in situ from a previously prepared high molecular weight acyclic backbone would afford a method for obtaining pure samples of p-polyphenylenes. In addition, such a synthetic route has the potential for producing a soluble prepolymer which could be fabricated before cyclization to the more rigid poly (p-phenylene).

The object of the current research effort is to develop a synthesis of p-polyphenyl model compounds of high purity via an in situ method which could be extended to the synthesis of high molecular weight poly (p-phenylene) polymers. The route chosen to accomplish the proposed synthesis involves the previously reported (Reference 3) base catalyzed rearrangement of allylpropynylammonium cations to 3-dimethylaminohept-5-en-1-yne which could then be thermally cyclized to the all para linked polyphenyl system of the desired chain length.

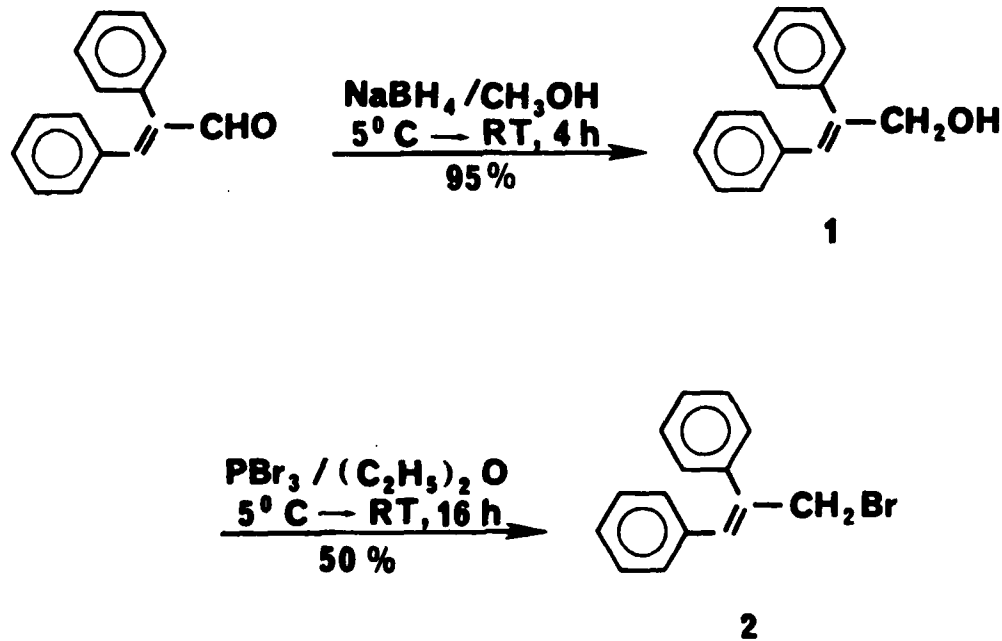
The synthetic method developed for the para linked model compounds would then be applied in future work to produce polyphenylene polymers containing a high degree of para oriented linkages.

SECTION II

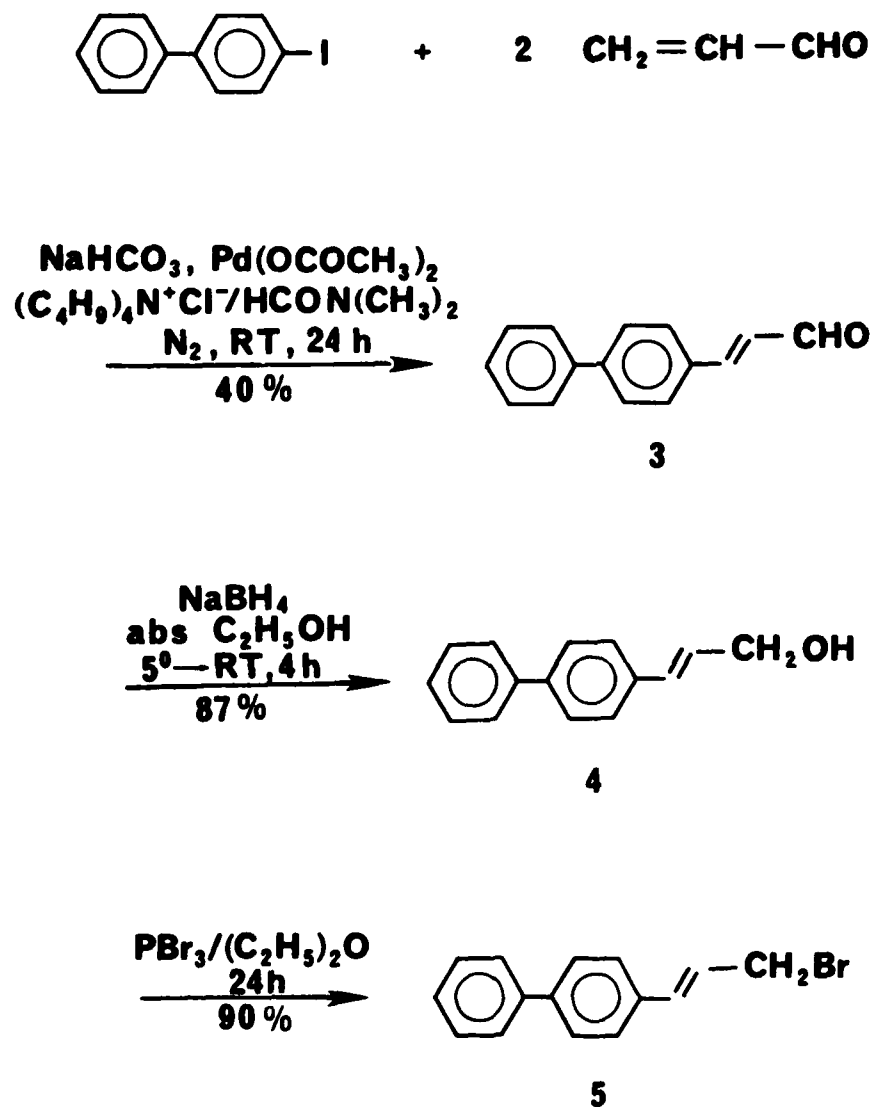
RESULTS AND DISCUSSION

1. Synthesis of Aryl Propenyl Bromides

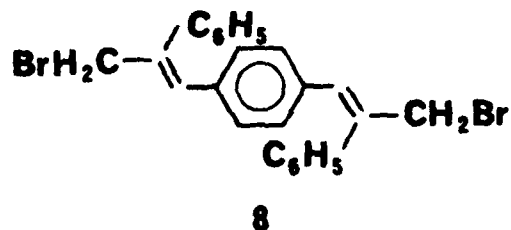
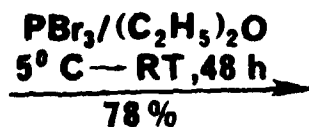
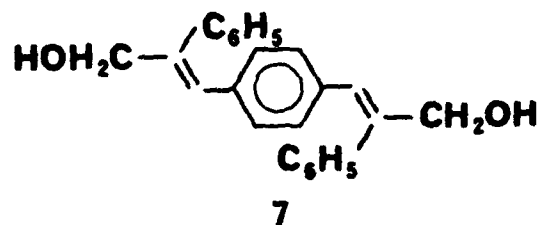
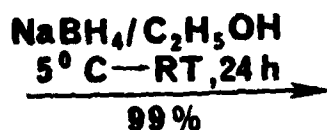
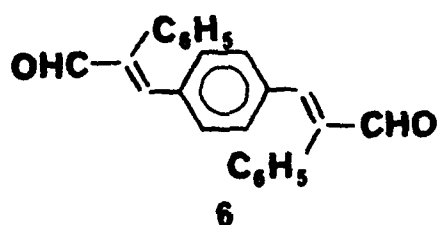
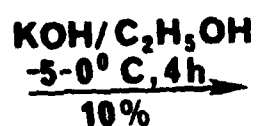
All the aryl propenyl bromide starting materials were prepared via the corresponding aldehyde and alcohol intermediates. The alcohol, (E)-2,3-diphenyl-2-propene-1-ol (1), was obtained with slight modifications of the known procedure (Reference 4) in 95% yield by the sodium borohydride reduction of the corresponding aldehyde (Reference 5). Treatment of 1 with phosphorous tribromide afforded the aryl propenyl bromide 2 in 50% yield (Reference 6).



The palladium catalyzed phase transfer reaction of 4-iodobiphenyl with acrolein was carried out using conditions similar to those described in the literature (Reference 7) to afford the resulting biphenyl olefinic aldehyde 3 in 40% yield. Reduction to form 4 followed by the standard treatment with phosphorus tribromide produced the desired bromide 5 in high yield.

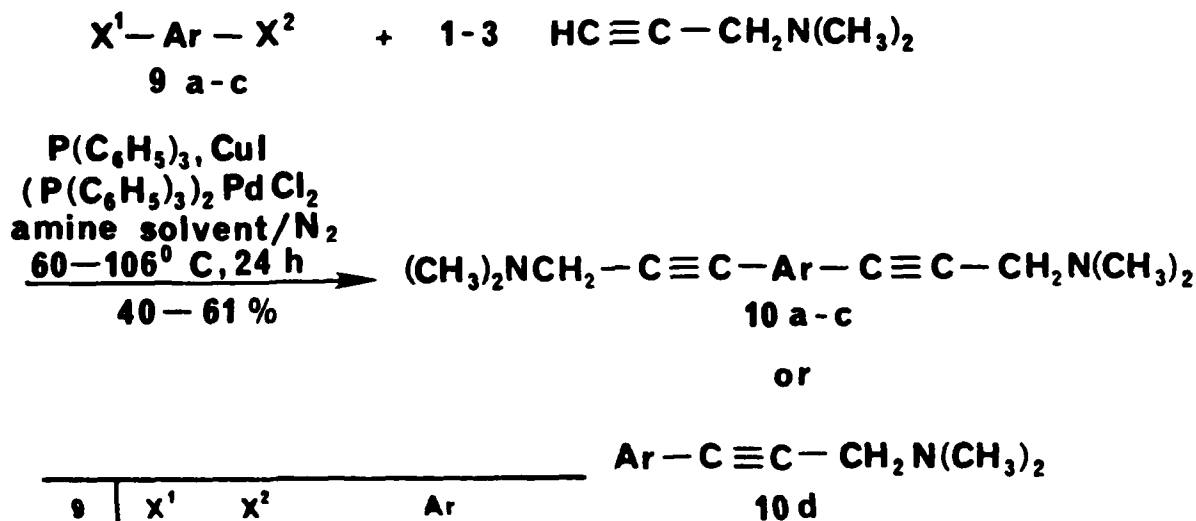


The dialdehyde 6 was synthesized in low yield (10%) via the crossed aldol condensation of phenylacetaldehyde with terephthalaldehyde. Treatment with sodium borohydride gave essentially a quantitative yield of the dialcohol 7. Conversion to the dibromide 8 was smoothly carried out as before with phosphorus tribromide in diethyl ether.



2. Synthesis of Aryl N,N-Dimethyl-2-propyn-1-amines 10a-d

The previously published method (Reference 8) for the synthesis of N,N-dimethyl-3-phenyl-2-propyn-1-amine was found to be unsatisfactory for the synthesis of the aryl N,N-dimethyl-2-propyn-1-amine starting materials. A one-step method, similar to one previously described (Reference 9) involving the palladium catalyzed substitution of halide by the alkyne functionality of N,N-dimethylamino-2-propyne gave the desired products 10a-d in moderate yield (40-61%). Piperidine is a superior solvent to triethylamine when using the more insoluble p-terphenyl halides. Analytical and spectroscopic data for the amines prepared are summarized in Tables 1 and 3.




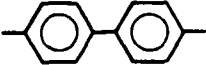


9	X ¹	X ²	Ar
a	I	I	
b	Br	Br	
c	I	I	
d	H	I	

Table 1. N,N-Dimethyl-(3-phenylprop-2-ynyl)amines 10a-d Prepared

Product No.	Solvent	Temp [°C]	Yield [%]	m.p. [°C] (b) (solvent)	Molecular formula (d)	I.R. (KBr) ν [cm ⁻¹] (e)	¹ H-NMR (CDCl ₃) δ [ppm] (f)	M.S. (70ev) m/z (%)
10a	triethyl-amine	60	45	44-45 ^o (c)	C ₁₆ H ₂₀ N ₂ (240.34)	1507, 1327, 1034, 835	2.35 (s, 12H); 3.45 (s, 4H); 7.35 (s, 4H)	240 (M ⁺ , 48); 42 (100)
10b	triethyl-amine	89	61	115-116 ^o (hexane)	C ₂₂ H ₂₄ N ₂ (316.43)	1492, 1324, 1035, 819	2.35 (s, 12H); 3.45 (s, 4H); 7.59 (s, 8H)	361 (M ⁺ , 57); 42 (100)
10c	piperidine	106	40	240-242 ^o dec (1 benzene:1 cyclohexane)	C ₂₈ H ₂₈ N ₂ (392.52)	1326, 1035, 825	2.40 (s, 12H); 3.52 (s, 4H); 7.70 (m, 12H)	392 (M ⁺ , 30); 42 (100)
10d	piperidine	85	54	209-211 ^o (1 toluene:1 hexane)	C ₂₃ H ₂₁ N (311.41)	1483, 1326, 1035, 824	2.40 (s, 6H); 3.52 (s, 2H); 7.70 (m, 13H)	311 (M ⁺ , 26); 42 (100)

(a) Yield of isolated product 10 based on 9.

(b) Uncorrected, measured on a Mel-Temp melting point apparatus.

(c) Purified by column chromatography on silica gel (8:1 diethyl ether:tetrahydrofuran).

(d) Satisfactory microanalyses obtained: C \pm 0.30, H \pm 0.10, N \pm 0.27.

(e) Recorded on a Beckman FT 1100 spectrophotometer.

(f) Recorded on a Varian EM-360A spectrometer.

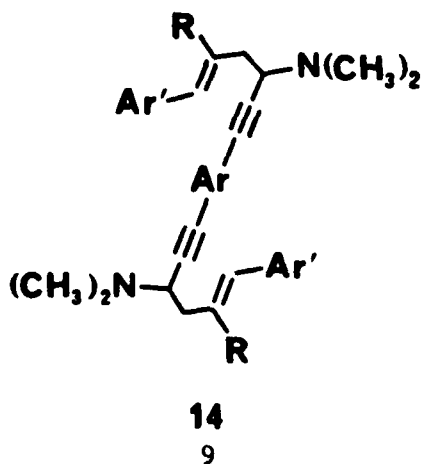
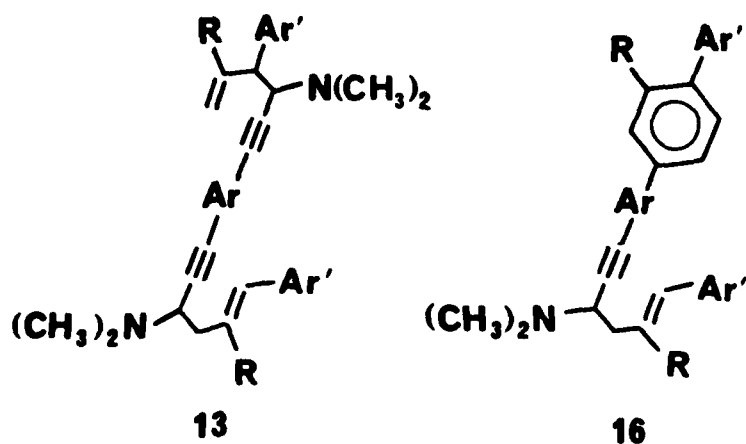
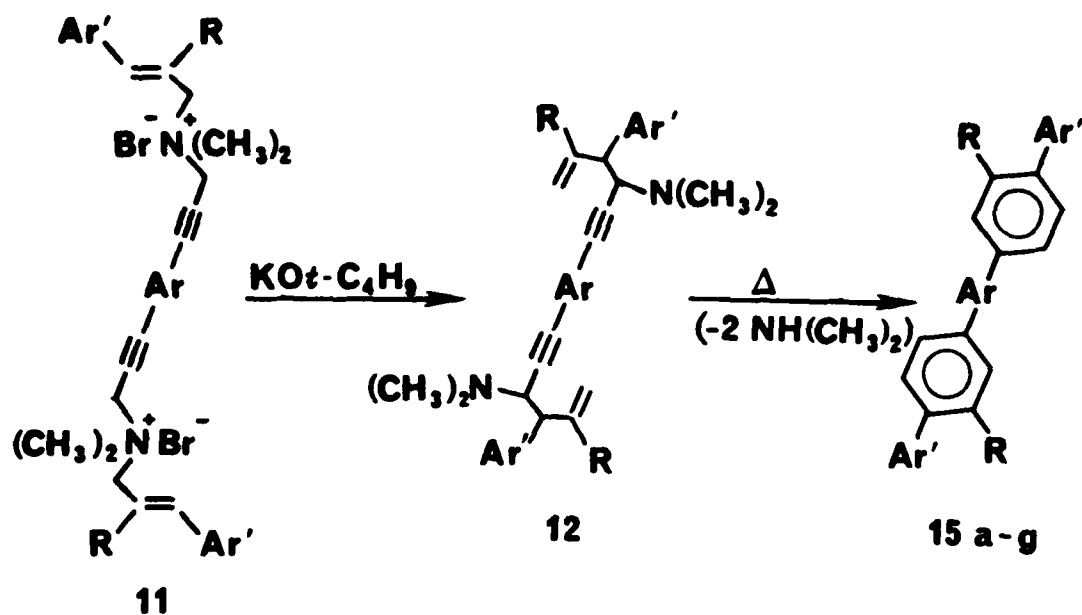
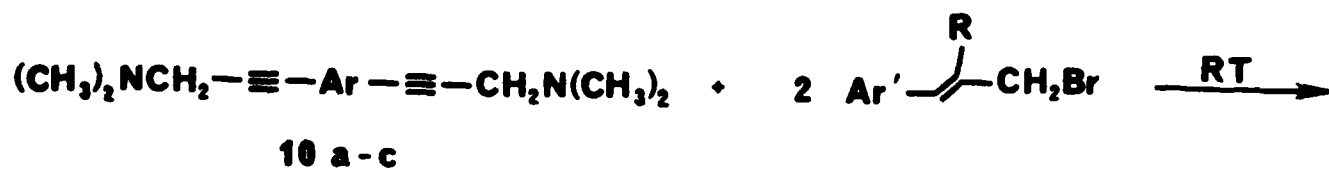
(g) Recorded on a Finnegan GC/MS/DS System Model 4021.


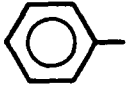


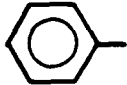

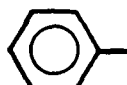


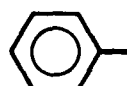

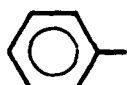


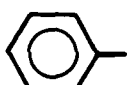

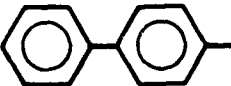
3. Polyphenyl Synthesis 15a-g, 21a-b

The syntheses of the *p*-polyphenyls were carried out employing a three-step, one-pot procedure starting from the appropriate aryl propenyl bromide and the corresponding aryl N,N-dimethyl-2-propyn-1-amine. Room temperature addition in triglyme afforded high yields of the bis ammonium salt 11.

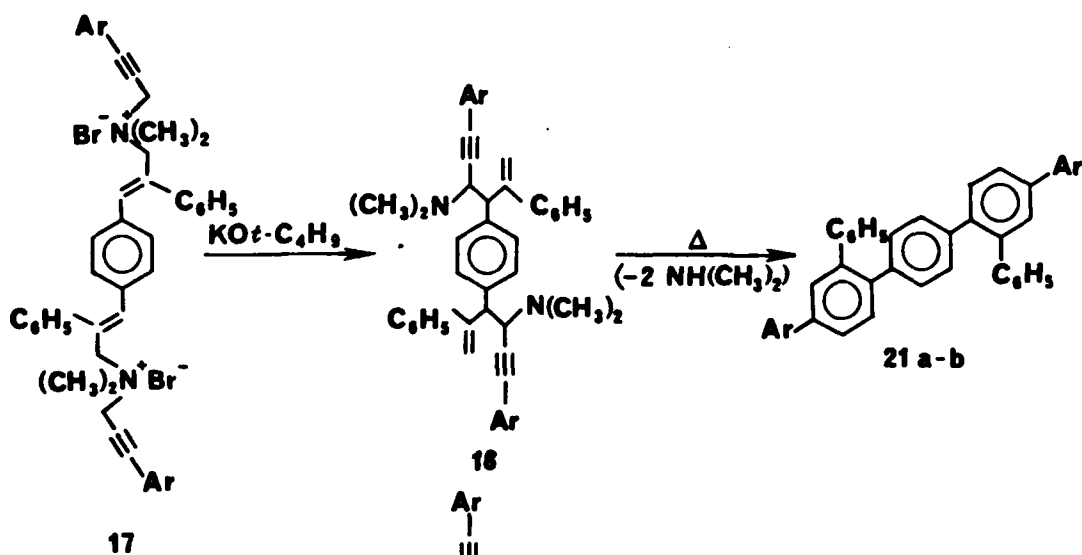
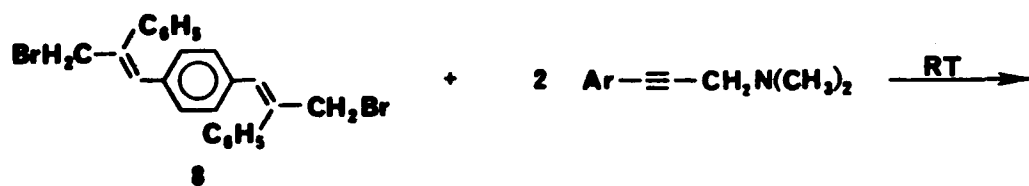
Upon treatment with potassium *t*-butoxide the ammonium salts undergo a Stevens rearrangement to three possible isomeric unconjugated enynes 12-14.

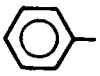
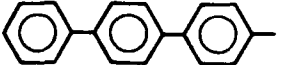
The reaction mixture containing the various isomers was then heated to 190°C at which temperature only the linkages containing terminal olefinic bonds aromatize. Due to extreme differences in solubility only the fully aromatized polyphenyls 15a-g precipitate from the reaction mixture with the partially closed 16 and unreacted 14 remaining in solution.



15	Ar	R	Ar'
a		H	
b			
c		H	
d			
e		H	
f			
g		H	

Polyphenyls containing pendant phenyl groups 21a-b were synthesized in an analogous manner. Analytical and spectroscopic data for all polyphenyls prepared are summarized in Tables 2 and 3. In all cases the products containing pendant phenyl groups exhibited increased solubility and lowered melting points when compared to their corresponding unsubstituted analogs. The p-septiphenyl 15e, p-octiphenyl 15g and the phenyl substituted p-noniphenyl 21b showed very limited solubility in boiling 1,2,4-trichlorobenzene and final purification could only be accomplished by vacuum sublimation or soxhlet extraction.



21	Ar
a	
b	

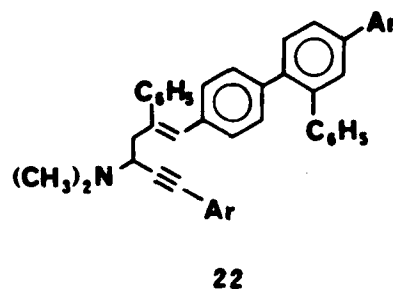
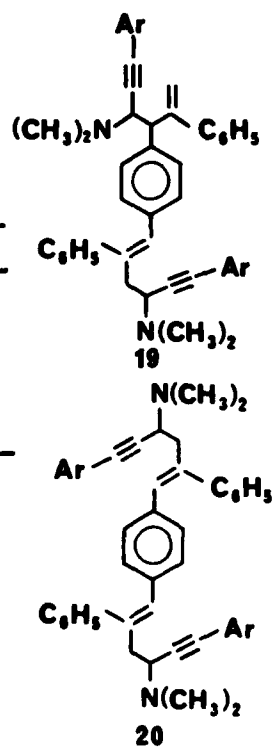


Table 2. p-Polyphenylenes 15a-g, 21a-b Prepared

Product No.	Yield %	m.p. [°C] (c) (solvent)	Molecular formula (g) or Lit. m.p. [°C]	I.R. (KBr) (h) ν [cm ⁻¹]	M.S. (70 eV) m/z (%) (k)
<u>15a</u>	42 (a)	388° (1,2,4-TCB) (d)	388 (Ref 10)	820.0 (j)	382 (M ⁺ , 100)
<u>15b</u>	19 (a)	288° (xylenes)	C ₄₂ H ₃₀ (534.66)	1473, 815, 764	534 (M ⁺ , 100); 267 (M ⁺⁺ , 99)
<u>21a</u>	29 (b)	255° (xylenes)	C ₄₂ H ₃₀ (534.66)	1473, 823, 763	534 (M ⁺ , 100); 267 (M ⁺⁺ , 7)
<u>15c</u>	46 (a)	437° (1,2,4-TCB)	429 (Ref 10) 475 (Ref 11)	815.0 (j)	458 (M ⁺ , 32); 229 (M ⁺⁺ , 100)
<u>15d</u>	62 (a)	341° (1,2,4-TCB)	C ₄₈ H ₃₄ (610.75)	1474, 814, 762	610 (M ⁺ , 68); 305 (M ⁺⁺ , 100)
<u>15e</u>	49 (a)	468° insoluble (e)	545 (Ref 11)	812.0 (j)	534 (M ⁺ , 100)
<u>15f</u>	39 (a)	375° (1,2,4-TCB)	C ₅₄ H ₃₈ (686.84)	1473, 813, 764	686 (M ⁺ , 100); 343 (M ⁺⁺ , 96)
<u>15g</u>	46 (a)	491° insoluble (f)	C ₄₈ H ₃₈ (610.75)	809.9 (j)	610 (M ⁺ , 21); 305 (M ⁺⁺ , 100)
<u>21b</u>	25 (b)	416° (1,2,4-TCB)	C ₆₆ H ₄₆ (839.02)	1473, 817, 766	839 (M ⁺ , 100); 419 (M ⁺⁺ , 12)

(ATTACHMENT TO TABLE 2)

- (a) Yield of isolated product 15 based on 10a-c.
- (b) Yield of isolated product 21 based on 8.
- (c) Measured by differential scanning calorimetry ($\Delta T=10^{\circ}\text{C}/\text{min}$) on a DuPont 910 DSC apparatus with Omnitherm 35053 three-module controller.
- (d) 1,2,4- Trichlorobenzene.
- (e) Purified by sublimation.
- (f) Purified by soxhlet extraction in boiling xylenes.
- (g) Satisfactory microanalyses obtained: $\text{C} \pm 1.30$, $\text{H} \pm 0.23$.
- (h) Recorded on a Beckman FT 1100 spectrophotometer.
- (j) Absorption defines C-H out-of-plane deformation of adjacent hydrogens on consecutively para-linked benzene rings (References 14,15).
- (k) Recorded on a Finnegan GC/MS/DS system Model 4021.

TABLE 3
MICROANALYSES OF PRODUCTS 10a-d, 15a-g and 21 a-b

PRODUCT NO.	CALCULATED (FOUND) ^(a)		
<u>10a</u>	C	79.95	(79.84)
	H	8.39	(8.41)
	N	11.66	(11.43)
<u>10b</u>	C	83.50	(83.80)
	H	7.60	(7.61)
	N	8.86	(9.10)
<u>10c</u>	C	85.67	(84.96)
	H	7.19	(7.22)
	N	7.14	(7.32)
<u>10d</u>	C	88.75	(88.51)
	H	6.75	(6.85)
	N	4.50	(4.77)
<u>15a</u>	C	94.20	(94.15) ^(b)
	H	5.80	(5.90)
<u>15b</u>	C	94.34	(94.36)
	H	5.66	(5.69)
<u>15c</u>	C	94.28	(94.23) ^(b)
	H	5.71	(5.86)
<u>15d</u>	C	94.39	(94.38) ^(b)
	H	5.61	(5.64)
<u>15e</u>	C	94.34	(93.43) ^(b)
	H	5.66	(5.89)
<u>15f</u>	C	94.42	(94.33) ^(b)
	H	5.58	(5.71)
<u>15g</u>	C	94.39	(93.09) ^(b)
	H	5.61	(5.75)
<u>21a</u>	C	94.34	(94.25) ^(b)
	H	5.66	(5.68)
<u>21b</u>	C	94.47	(93.21) ^(b)
	H	5.53	(5.66)

(a) Analyses performed for C, H, N on a Perkin-Elmer Elemental Analyzer Model 240C.

(b) WO₃ added as a combustion aid.

SECTION III

EXPERIMENTAL

All amine solvents, commercially available, were distilled and stored over molecular sieves (Linde, 4A) before use. The following reagents were obtained from Aldrich Chemical Co. and were used without further purification:

1,2,4-trichlorobenzene (99%), triglyme (99%), 1,4-diiodobenzene (98%, 9a, $X^1=X^2=I$,), 4,4'-dibromobiphenyl (98%, 9b, $X^1=X^2=Br$,), and 3-bromo-1-phenyl-1-propene (technical grade).

(E)-2,3-Diphenyl-2-propene-1-ol (1):

The alcohol 1 is prepared by modification of a known procedure (Reference 4) in which sodium borohydride (3.11g, 82.0 mmol) is added in increments over a 5-min period to a suspension of (E)-2,3-diphenyl-2-propenal(Reference 5) (17.05g, 82.0 mmol) in cold (5°C) methanol (400 ml). The flask is allowed to warm to room temperature and is stirred for 4 h. The pure product 1 is obtained by precipitation of the colorless solution into water (1000 ml) to give white needles: 16.07g (95%); m.p. 72-73°C [Reference 4, m.p. 68-69°C].

(E)-1,1'-[1-(Bromomethyl)-1,2-ethenediyl]bis[benzene] (2):

A solution (Reference 6) of phosphorous tribromide (6.99g, 25.8 mmol) in diethyl ether (30 ml) is added dropwise over a period of 20 min to a cold (5°C) solution of alcohol 1 (16.25g, 77.4 mmol) in diethyl ether (200 ml). The flask

is warmed to room temperature and stirred for 16 h. The solution is poured into 5% aqueous sodium hydroxide and the ethereal layer is separated from the base. After washing with water (2 X 1200 ml), the ether is removed by distillation to give a yellow oil consisting of crude product. Pure product 2 is isolated by chromatography on a silica gel column (Woelm DCC, 5cm dia X 60cm H) using petroleum ether/dichloromethane (4:1) as the eluent and the drying of similar fractions of eluate in a warm oven (50°C) at reduced pressure (30mm Hg) to afford a light-yellow oil: 10.50g (50%).

$C_{15}H_{13}Br$ calc. C 65.93 H 4.76 Br 29.30

(273.2) found 67.46 4.91 29.46

1H -N.M.R. ($CDCl_3/TMS_{int}$, 60 MHz): δ 4.40 (s, 2H, $-CH_2-$); 7.10(s, 1H, H); 6.40-7.50 ppm (m, 10H_{arom}) (Figure 1).

I.R.(neat) ν 3080, 3060, 3010, 2950, 1600, 1560, 1200, 765, 750, 690 cm^{-1} (Figure 10).

E.I.M.S. [70 eV]: m/z =274 (M^+ , 6, ^{81}Br), 272 (M^+ , 6, ^{79}Br), 193 (100).

(E)-3-(1,4-Biphenyl)-2-propenal (3):

The aldehyde 3 is prepared by modification of a known procedure (Reference 7) in which a mixture of 4-iodobiphenyl (Aldrich, 10.00g, 35.7 mmol), acrolein (Aldrich, 4.03g, 71.9 mmol), sodium bicarbonate (7.56g, 90.0 mmol), tetra-n-butylammonium chloride (Aldrich 96%, 11.60g, 41.7 mmol), and palladium acetate (Strem, 2.24g, 10.0 mmol) in degassed N,N-dimethylformamide (100 ml) is stirred at room temperature under nitrogen for 24 h. The mixture is poured into water (700 ml) and the resulting precipitate is filtered and air dried. The precipitate is stirred vigorously in boiling heptane (600 ml) for 15 min and filtered hot. The pure product 3 is afforded as a light-yellow solid upon cooling of the filtrate to room temperature: 3.00g (40%); m.p. 110-112°C.

$C_{15}H_{12}O$ calc. C 86.51 H 5.81

(208.3) found 86.30 5.91

$^1\text{H-N.M.R.}$ ($\text{CDCl}_3/\text{TMS}_{\text{int}}$, 60 MHz): δ 6.55–7.00 (m, 2H, $-\text{CH}=\text{CH}-$); 7.40–7.80 (m, 9H_{arom}); 9.85 ppm (d, 1H, CHO, $J=8.5$ Hz) (Figure 2).

E.I.M.S. [70 eV]: $m/z=208$ (M^+ , 100).

(E)-2,3-Diphenyl-2-propene-1-ol (4):

The alcohol 4 is prepared in a manner similar to 1 using aldehyde 3 (4.00g, 19.2 mmol), sodium borohydride (0.36g, 9.5 mmol) and absolute ethanol (40 ml). Upon recrystallization from isopropanol/water (3:1) (200 ml) pure product 4 is afforded as a white powder: 3.52g (87%); m.p. 161–162°C.

$\text{C}_{15}\text{H}_{14}\text{O}$ calc. C 85.68 H 6.71

(210.3) found 85.42 6.80

$^1\text{H-N.M.R.}$ ($\text{CDCl}_3/\text{TMS}_{\text{int}}$, 60 MHz): δ 3.15 (s, 1H, OH); 4.25 (d, 2H, CH_2 , $J=4$ Hz); 6.40–6.48 m, 2H, $-\text{CH}=\text{CH}-$; 7.40–7.80 ppm (m, 9H_{arom}) (Figure 3).

E.I.M.S. [70 eV]: $m/z=210$ (M^+ , 89), 167 (100).

(E)-1-[1-(Bromomethyl)-1,2-ethenediyl]-4-biphenyl (5):

Phosphorous tribromide (288g, 10.6 mmol) in anhydrous diethyl ether (5 ml) is added dropwise over a period of 15 min to a cold (5°C) suspension of alcohol 4 (3.85g, 18.3 mmol) in diethyl ether (50 ml). The flask is allowed to warm to room temperature and stirred for 24 h. The product 5 is obtained from precipitation of the ethereal solution into water (400 ml) and recrystallization of the resulting solid from hexane (100 ml):

4.42g (90%); m.p. 130–131°C.

$\text{C}_{15}\text{H}_{13}\text{Br}$ calc. C 65.95 H 4.80 Br 29.25

(273.2) found 67.77 4.80 29.06

$^1\text{H-N.M.R.}$ ($\text{CDCl}_3/\text{TMS}_{\text{int}}$, 60 MHz): δ 4.20 (d, 2H, CH_2 , $J=6$ Hz); 6.40–6.65 (m, 2H, $-\text{CH}=\text{CH}-$); 7.45–7.85 ppm (m, 9H_{arom}) (Figure 4).

E.I.M.S. [70 eV]: $m/z=274$ (M^+ , 4, ^{81}Br ; 272 (M^+ , 4, ^{79}Br); 193 (100).

(E,E)-3,3-[1,4-Phenylene]bis[2-phenyl-2-propenal] (6):

Potassium hydroxide (56.00g, 1.0 mol) is dissolved in absolute ethanol (2.4 l) in a 5.0 l three-necked roundbottom flask fitted with a mechanical stirrer and nitrogen inlet. The flask is cooled to 20°C by ice bath under a nitrogen atmosphere and terephthaldehyde (200.00g, 1.5 mol) is added to the solution. The mixture is then further cooled (-5°C) in a salt-ice bath for 30 min before the dropwise addition of phenylacetaldehyde (396.00g, 3.3 mol) over a 2 h period. The reaction is stirred under nitrogen for an additional 2 h maintaining the temperature at -5 to 0°C . The bright-yellow precipitate is filtered from the solution, washed with ethanol (0.56 l), hexane (0.5 l), and air dried to afford the crude product 6 (120.00g, 19%). Upon treatment with decolorizing carbon (5.00g) the product is recrystallized twice from ethyl acetate (4 l) to give 6 as small yellow plates: 43.00g (10%); m.p. $198\text{--}199^\circ\text{C}$.

$\text{C}_{24}\text{H}_{18}\text{O}_2$ calc C 85.18 H 5.36

(338.4) found 84.91 5.52

I.R. (KBr): ν 3080, 3060, 2830, 2720, 1665, 1660, 1395 cm^{-1} (Figure 11).

$^1\text{H-N.M.R.}$ ($\text{CD}_2\text{Cl}_2/\text{TMS}_{\text{int}}$, 60 MHz): δ 1.4 s, 2H, $-\text{CH}=\text{CH}-$; 6.50–7.10 (m, 14H_{arom}); 9.30 ppm (s, 2H, CHO) (Figure 5).

E.I.M.S. [70 eV]: $m/z=338$ (M^+ , 100).

(E,E)-3,3-[1,4-Phenylene]bis[2-phenyl-2-propene-1-ol] (7):

Sodium borohydride (2.81g, 74.0 mmol) is added in increments over a 5-min

period to a cold (5°C) suspension of aldehyde 6 (25.00g, 74.0 mmol) in absolute ethanol (220 ml). The flask is warmed to room temperature and stirred for 24 h. The reaction is precipitated into water (1500 ml) and the precipitate is collected on a Buchner funnel. After drying in a 100°C oven at reduced pressure 7 is afforded as a white powder which is used without further purification: 25.00g (99%); m.p. 195-196°C.

$C_{24}H_{22}O_2$ calc. C 84.18 H 6.48
(342.5) found 83.88 6.48

(E,E)-1,4-Bis(3-bromo-2-phenyl-1-propenyl)benzene (8):

Phosphorous tribromide (5.28g, 19.5 mmol) in anhydrous diethyl ether (30 ml) is added dropwise over a period of 15 min to a cold (5°C) suspension of bis-alcohol 7 (10.00g, 29.2 mmol) in diethyl ether (350 ml). The flask is warmed to room temperature and stirred for 48 h. The resulting white precipitate is collected on a Buchner funnel, and dried in a 100°C oven at reduced pressure (30-mm Hg) to give 8 as a white powder which is used without purification: 10.76g (78%); m.p. 141-142°C.

$C_{24}H_{20}Br_2$ calc. C 61.54 H 4.27 Br 34.19
(468.3) found 61.53 4.28 34.19

E.I.M.S. [70 eV]: m/z=470 (M^+ , 3, $^{81}Br^{81}Br$); 468 (M^+ , 4, $^{81}Br^{79}Br$); 466 (M^+ , 2, $^{79}Br^{79}Br$); 307 (100).

4,4''-Diiodo-1,4':1',1''-terphenyl (9c) and 4-iodo-1,4':1'1''-terphenyl (9d):

A mixture of p-terphenyl (Aldrich 4.60g, 20.0 mmol), iodine (4.05g, 16.0 mmol), and periodic acid (Aldrich 98%, 1.83g, 8.0 mmol) in a solvent mixture of acetic acid/water/sulfuric acid (10:2:0.3) (75 ml) is heated to 100°C by oil bath and stirred mechanically for 24 h. After cooling to room temperature (20-25°C) the

precipitate is collected and washed with 10% sodium bisulfite (500 ml). The crude products are stirred in refluxing toluene (250 ml) for 15 min and filtered hot. The insoluble product 9c is purified by two additional extractions with boiling toluene (2x250 ml) and dried to afford a white solid: 3.00g (31%); m.p. 307-309°C (dec.) [Reference 14, m.p. 307°C (dec.)].

$C_{18}H_{12}I_2$ calc. C 44.84 H 2.51 I 53.27
(482.1) found 44.81 2.55 52.36

E.I.M.S. [70 eV]: m/z=482 (M^+ , 14), 226 (100).

The toluene extracts are combined and concentrated to 33% of the original volume. Upon cooling to room temperature the precipitate is collected and purified by recrystallization in toluene (250 ml) to give 9d as a white solid: 4.50g (63%); m.p. 246-247°C [Reference 15, m.p. 246-247°C].

3,3'-Aryl-diylbis(N,N-dimethyl-2-propyn-1-amines) 10a-c; Typical Procedure:

The appropriate dihalo arene 9a-c (101.7 mmol) and 1-dimethylamino-2-propyne (Aldrich 98%, 310.6 mmol) in the designated amine solvent (1000 ml) are degassed for 30 min at room temperature before the addition of

triphenylphosphine (Aldrich 99%, 3.8 mmol), cuprous iodide (Alfa 98%, 1.1 mmol), and dichlorobis(triphenylphosphine) palladium (II) (Strem, 1.0 mmol).

The flask is heated for 24-48 h and allowed to cool to room temperature. The precipitate of ammonium halide salts is filtered from solution and washed with amine solvent (200 ml). The solvent is reduced to one quarter of the original volume by distillation under vacuum. The resulting concentrated solution is then poured into 5% hydrochloric acid (1000 ml) and the solution is adjusted to pH 9 by addition of 5% aqueous sodium hydroxide. The suspension is extracted with dichloromethane (3x300 ml) and separated. After drying over anhydrous magnesium sulfate (10.00g) the pure product 10a-c is afforded upon distillation

of the solvent and subsequent recrystallization (Table 1 and Figures 6-8, 12-14).

3-(1,4:1',4'-Terphenyl)-N,N-dimethyl-2-propyn-1-amine (10d):

The assymetric N,N-dimethyl-2-propyn-1-amine 10d is prepared in a manner similar to 10a-c by reaction of 4-iodo-1,4':1',1''-terphenyl (9d, $X^1=H$, $X^2=I$, 5.00g, 14.0 mmol) and 1-dimethylamino-2-propyne (Aldrich 98%, 1.75g, 21.1 mmol) in a degassed solution of piperidine (70ml) (Table 1 and Figures 9, 15).

para-Polyphenylenes 15a-g; General Procedure:

A suspension of the bis amine 10a-c (1.0 mmol) in triglyme (50 ml) is degassed for 20 min before the addition of 2, 5, or 3-bromo-1-phenyl-1-propene (2.0 mmol). The reaction mixture is stirred at room temperature (20-25°C) under nitrogen for 24 h. Anhydrous potassium-t-butoxide (2.0 mmol) is added to the solution and stirring is continued at room temperature under nitrogen for an additional 24 h. The temperature of the reaction mixture is raised to 190°C under nitrogen for 24 h and cooled to room temperature. The precipitate is filtered from solution through a Buchner funnel, washed with methanol (50 ml), distilled water (500 ml), and air dried. The product 15a-g is purified via either sublimation or recrystallization (Table 2 and Figures 16-22).

para-Polyphenylenes 21a-b; General Procedure:

The polyphenylenes 21a-b are prepared in a manner similar to the preparation of 15a-g by the reaction of (E,E)-1,4-bis(3-bromo-2-phenyl-1-propenyl)benzene (8) (1.0 mmol) with either N,N-dimethyl-3-phenyl-2-propyn-1-amine⁸ or 10d (2.0 mmol) (Table 2 and Figures 23-24).

REFERENCES

1. G. K. Noren, J. K. Stille, J. Polym. Sci. D: Macromol. Rev., 5, 385 (1971).
2. J. G. Speight, P. Kovacic, F. W. Koch, J. Macromol. Sci. Rev. Macromol. Chem., 5, 295 (1971).
3. T. Jemison, T. Laird, W. D. Ollis, I. O. Sutherland, J. Chem. Soc. Perk. I, 1436 (1980).
T. Laird, W. D. Ollis, I. O. Sutherland, J. Chem. Soc. Perk. I, 1473 (1980).
4. H. E. Zimmerman, L. Singer, B. S. Thyagarian, J. Am. Chem. Soc., 81, 108 (1959).
5. K. Alder, J. Haydin, K. Heinbach, K. Neufang, Ann., 586, 128 (1954).
6. A. Padwa, L. Brodsky, S. Clough, J. Am. Chem. Soc., 94, 6767 (1972).
7. T. Jeffery, J. Chem. Soc., Chem. Commun., 1287 (1984).
8. I. Iwai, T. Hiroaka, Chem. Pharm. Bull. (Japan), 11, 1564 (1963).
9. S. Takahashi, Y. Kuroyama, N. Sonogashira, N. Hagihara, Synthesis, 627 (1980).
10. H. Kambe, I. Mita, R. Yokota, Thermal Anal., 3, 387 (1971).
11. M. Busch, W. Weber, C. Darbouen, W. Renner, H. J. Hahn, G. Mathauser, G. Stratz, K. Zitzmann, H. Engelhardt, J. Prakt. Chem., 146, 1 (1963).
12. R. C. Doss, P. W. Solomon, J. Org. Chem., 29, 1567 (1964).
13. S. Sandroni, F. Geiss, Z. Anal. Chem., 220, 321 (1966).
14. A. N. Novikov, T. A. Khalimova, Obshchestva im. D. I. Mendeleeva, 7, 234 (1962); C.A., 57: 2385 f (1963).
15. H. France, I. M. Heilbron, D. H. Hey, J. Chem. Soc., 1364 (1938).

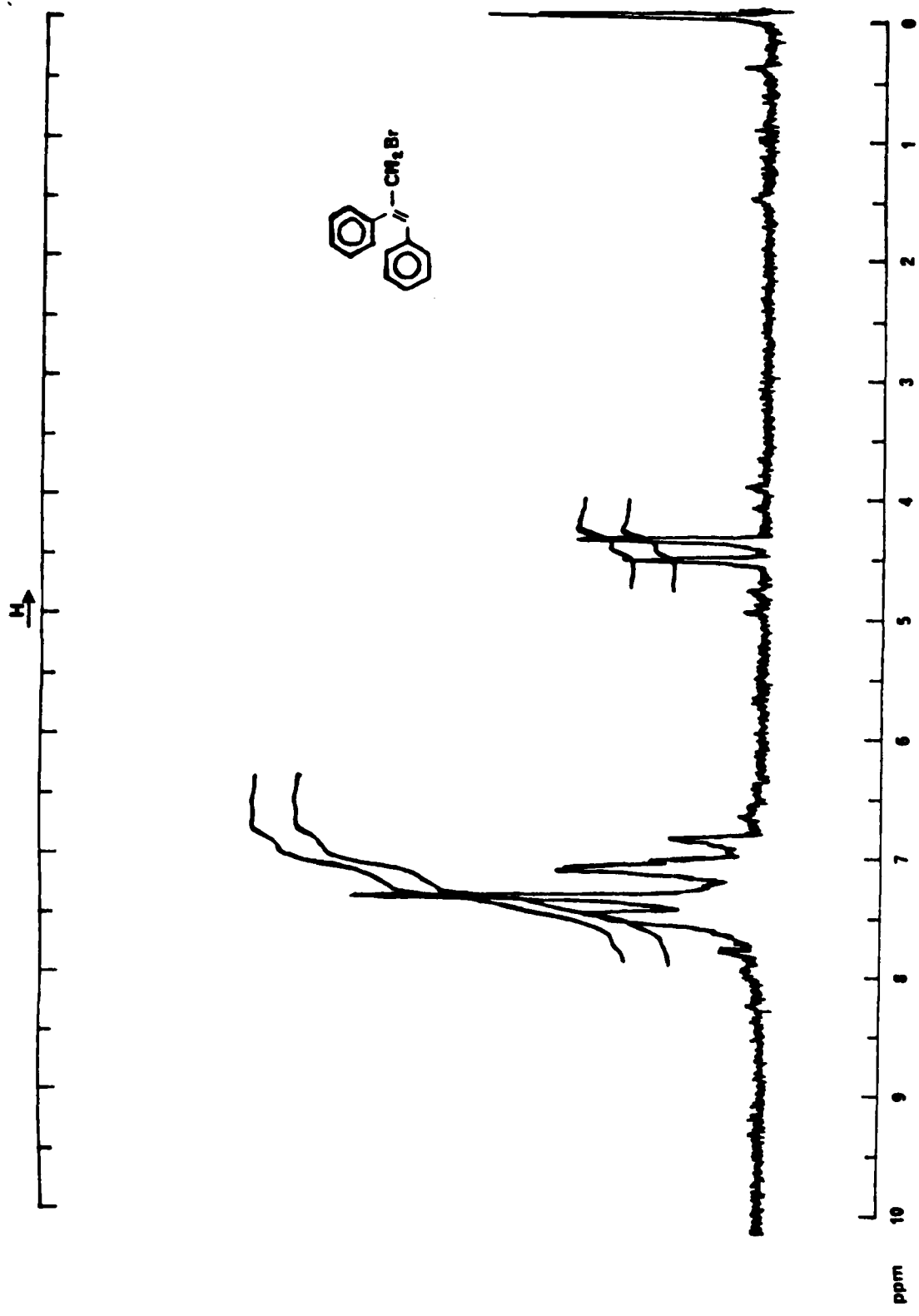


Figure 1. ^1H NMR Spectrum of Compound 2.

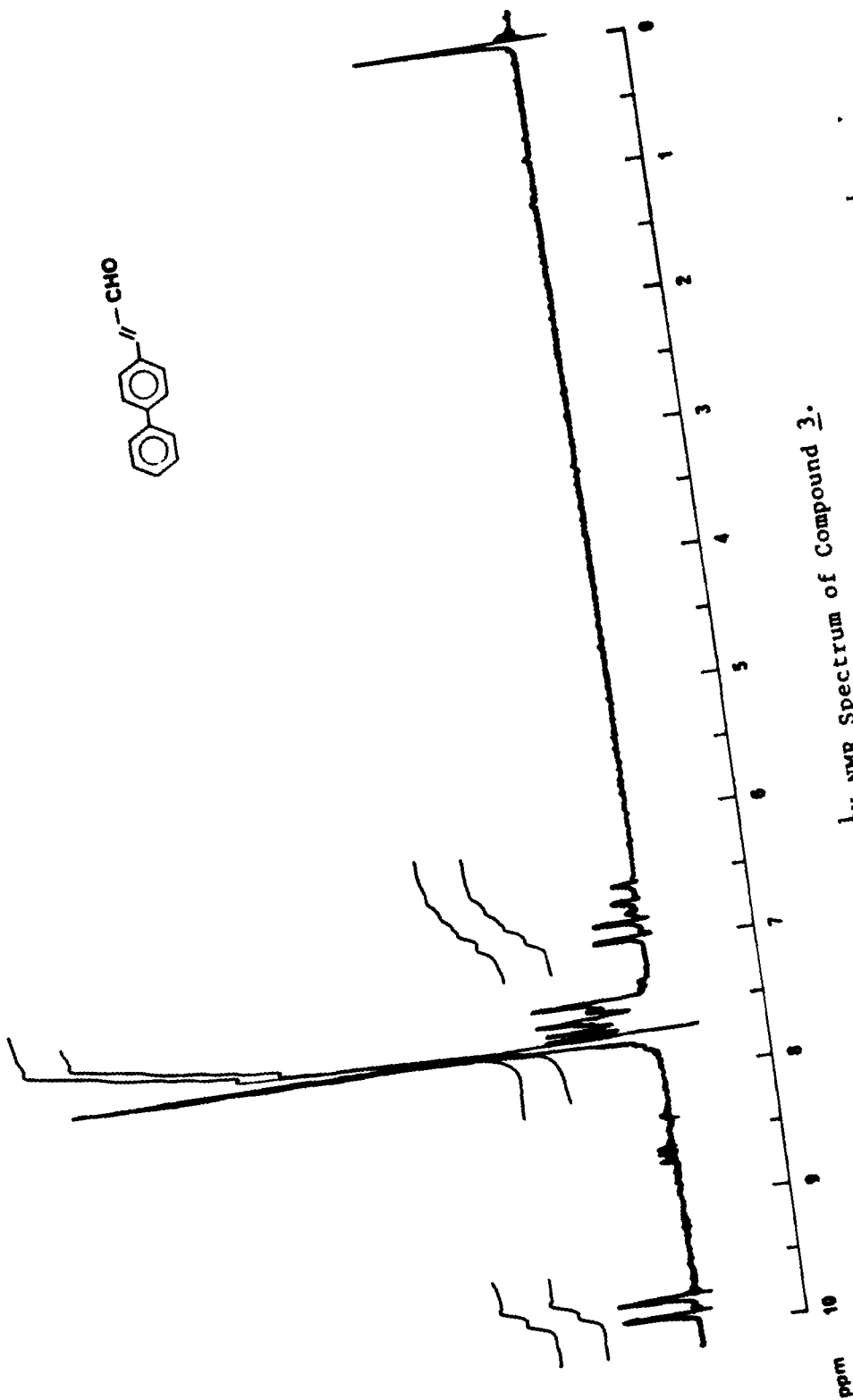
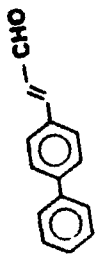
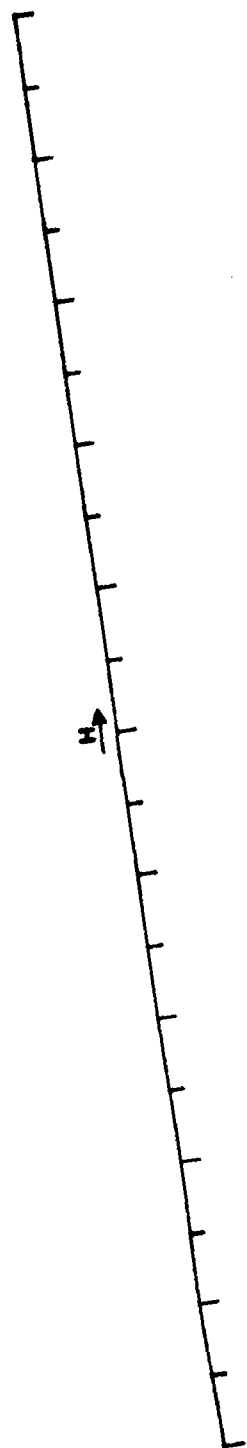


Figure 2. ^1H NMR Spectrum of Compound 3.

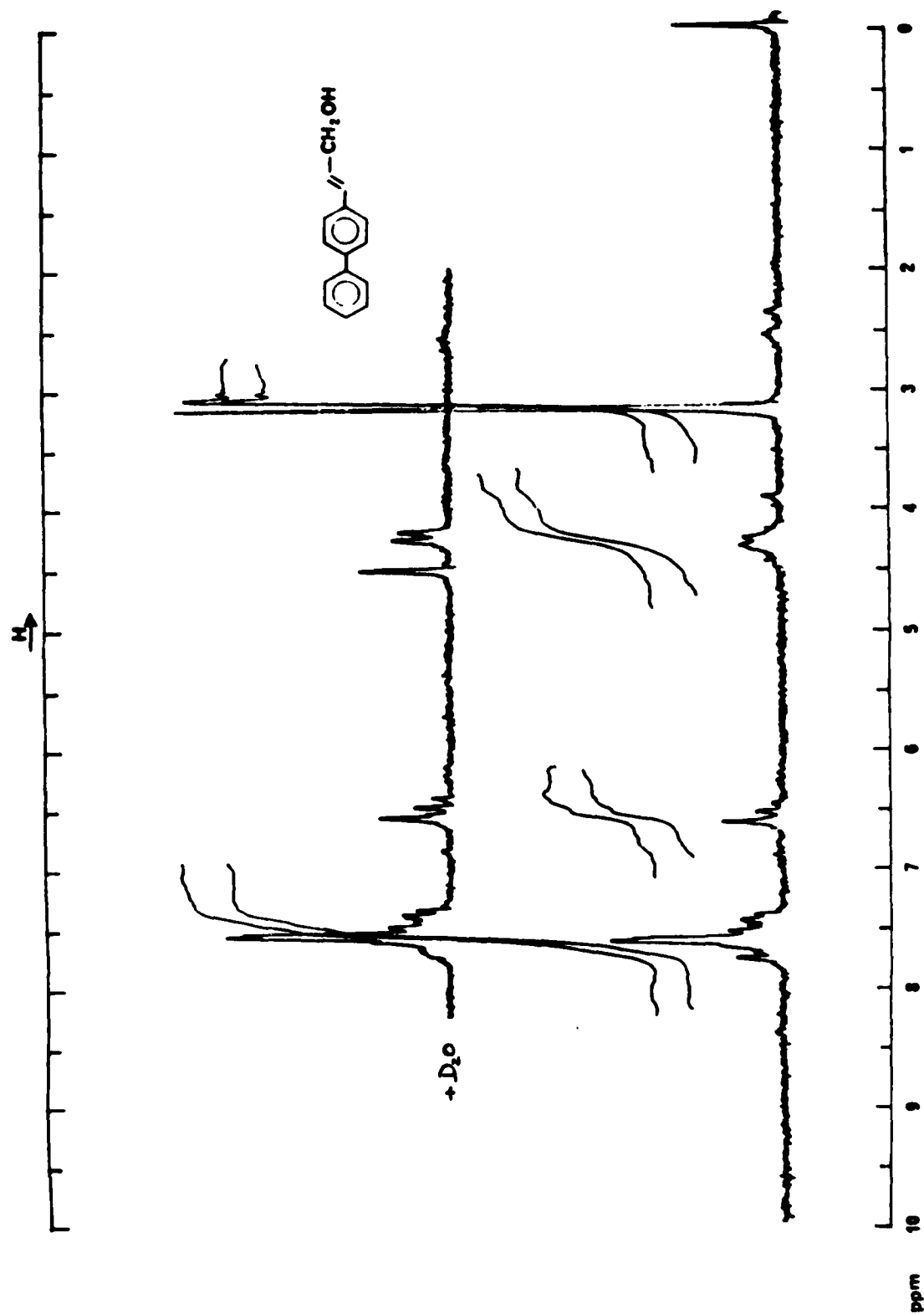


Figure 3. ¹H NMR Spectrum of Compound 4.

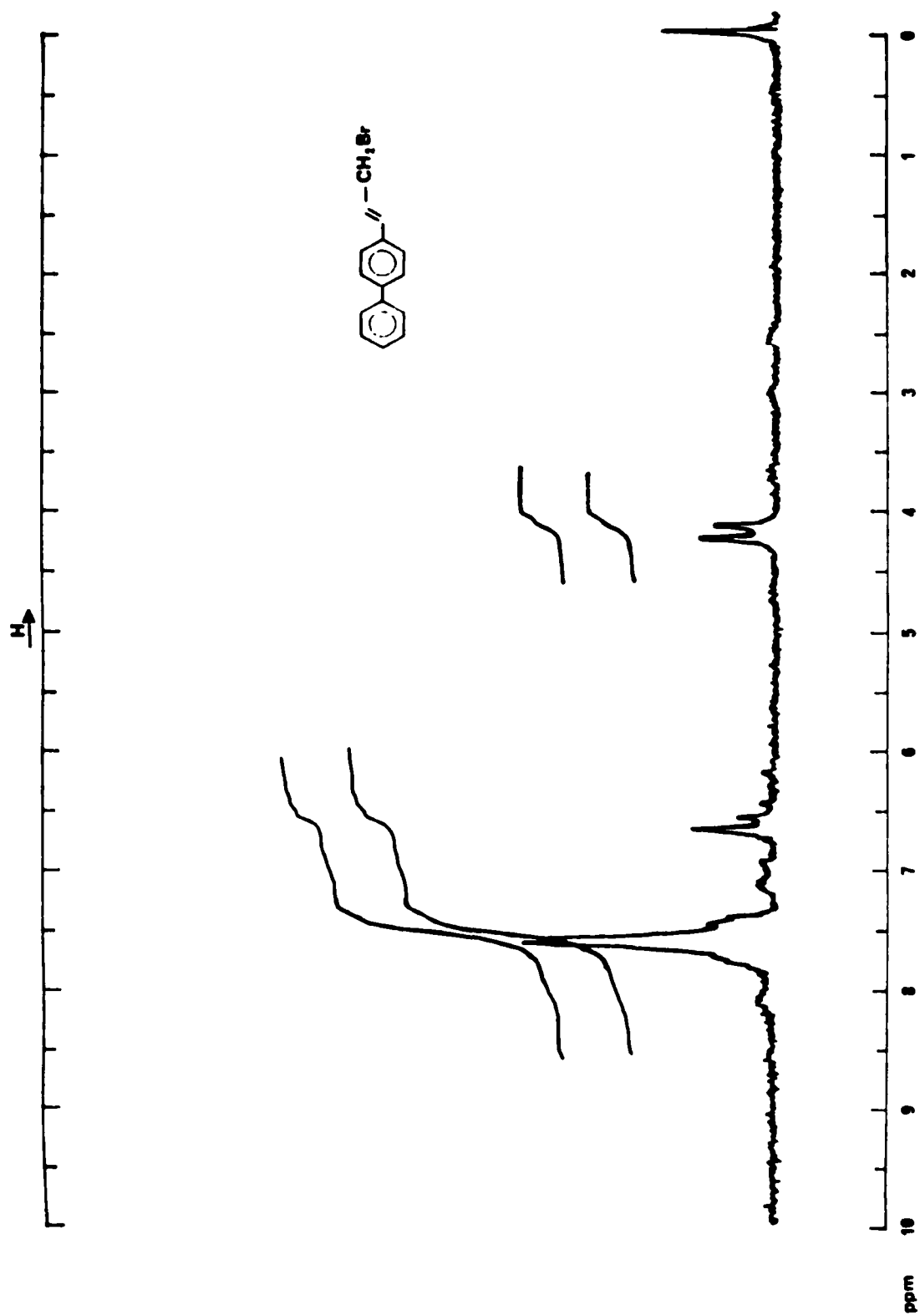


Figure 4. ^1H NMR Spectrum of Compound 5.

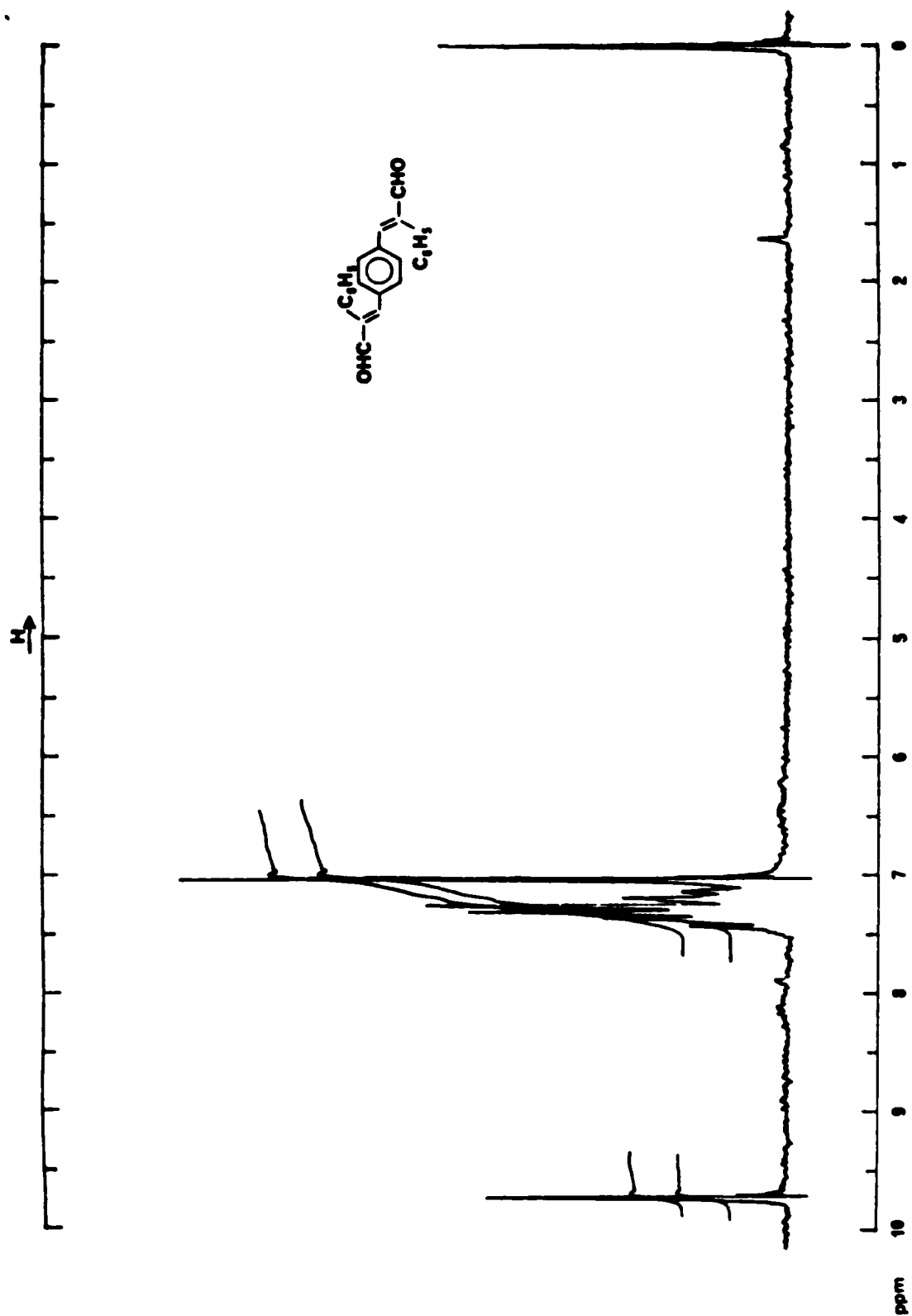


Figure 5. ^1H NMR Spectrum of Compound 6.

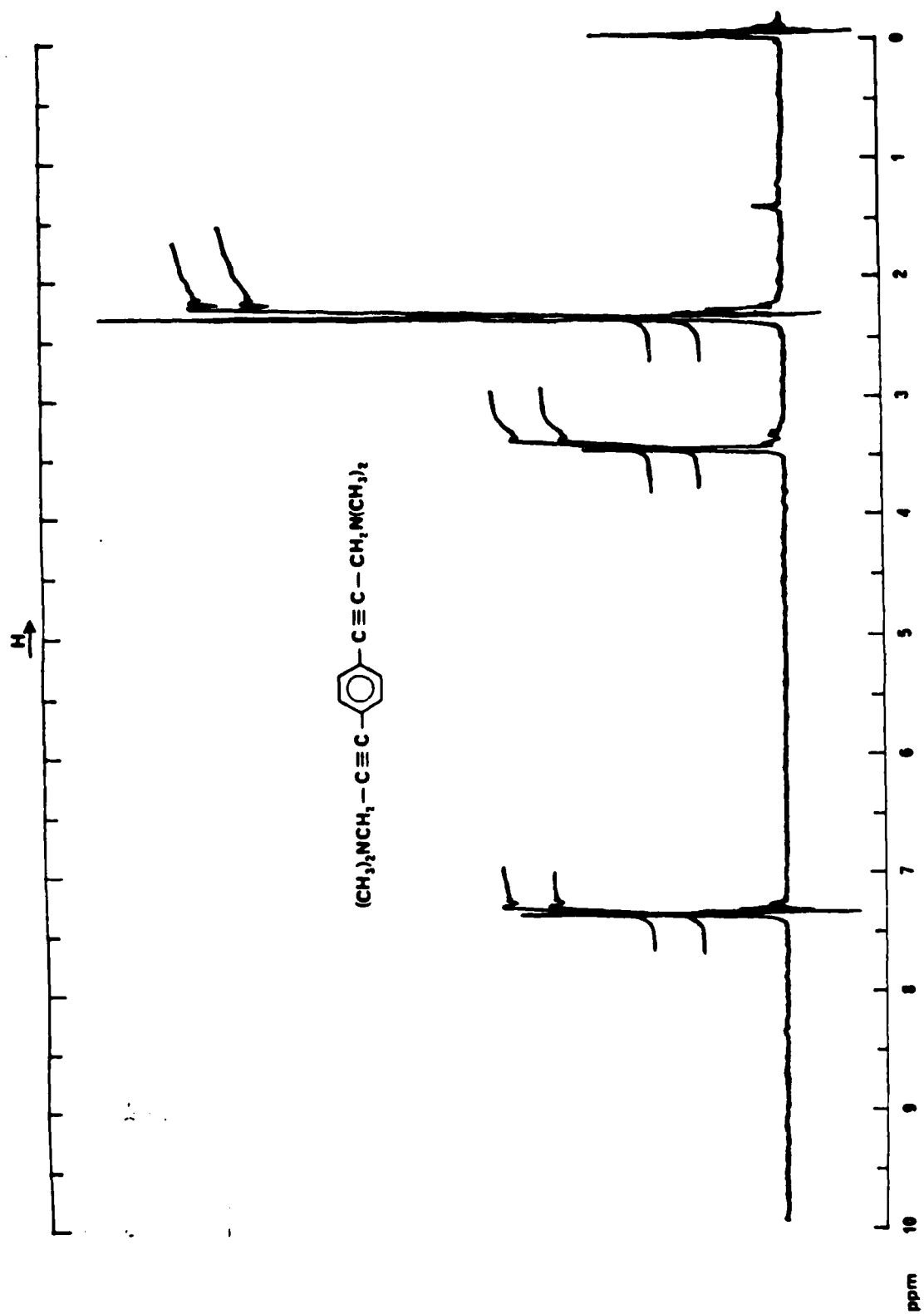


Figure 6. ^1H NMR Spectrum of Bisamine 10a.

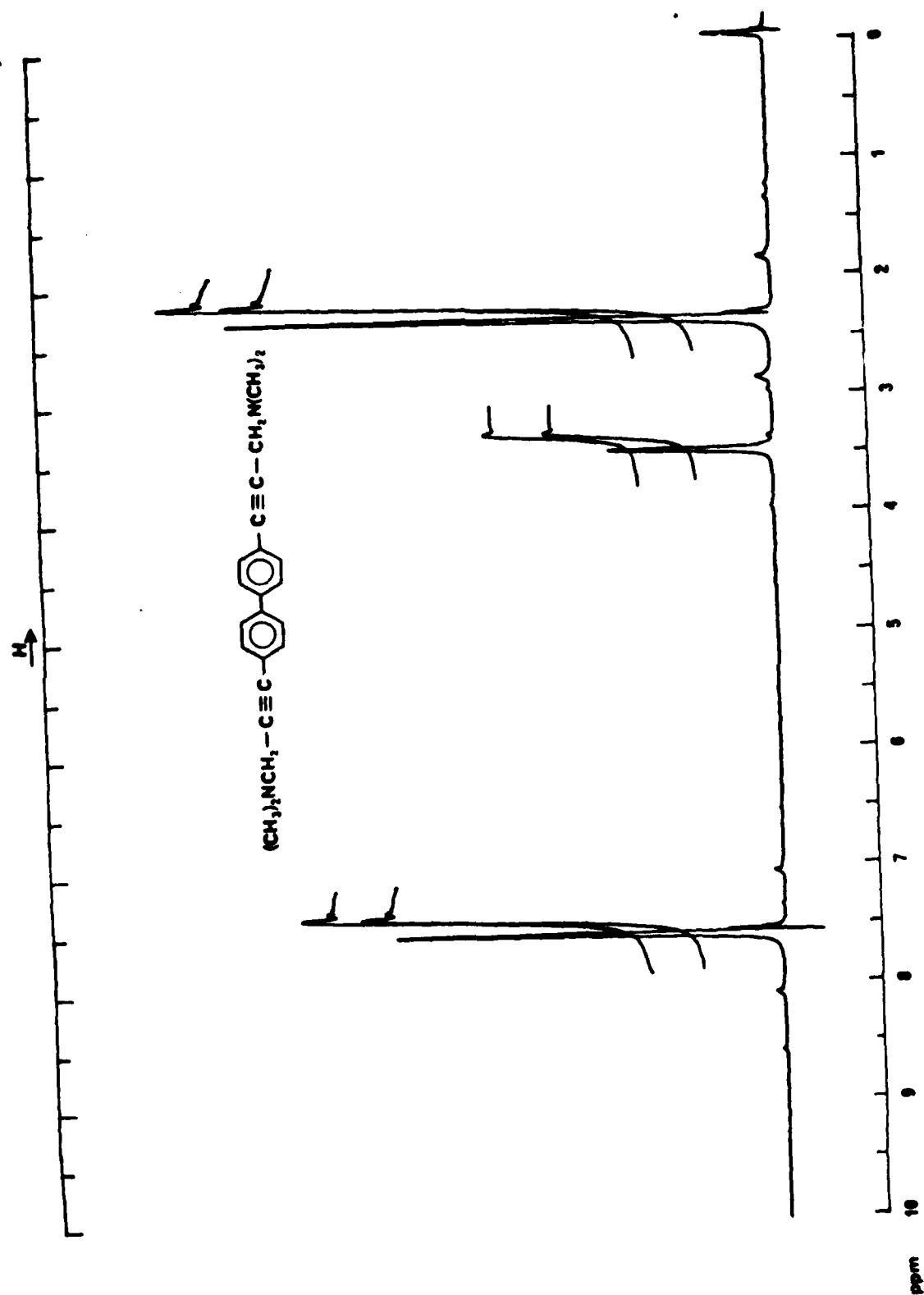


Figure 7. ^1H NMR Spectrum of Bisamine 10b.

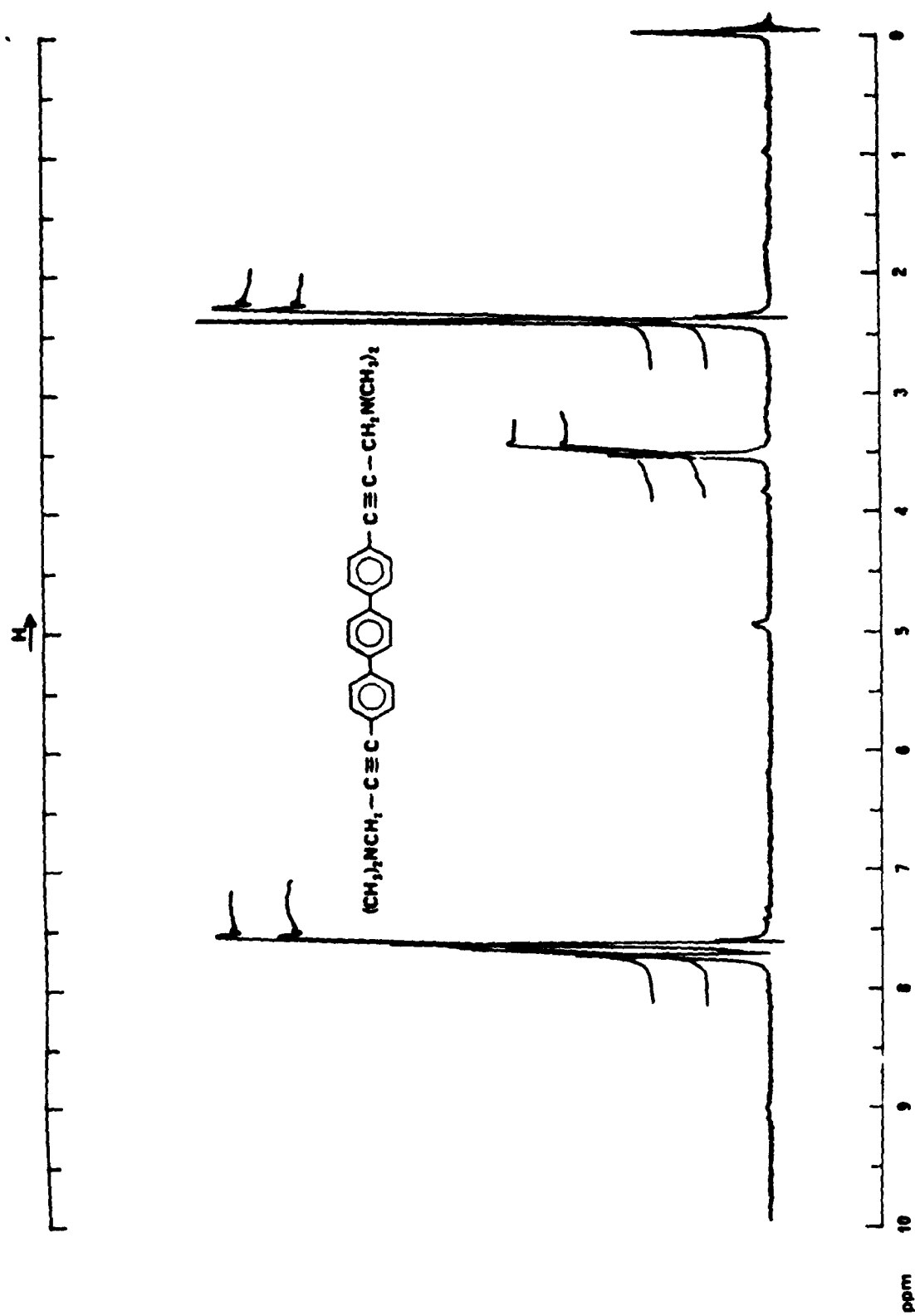


Figure 8. ^1H NMR Spectrum of Bisamine 10c.

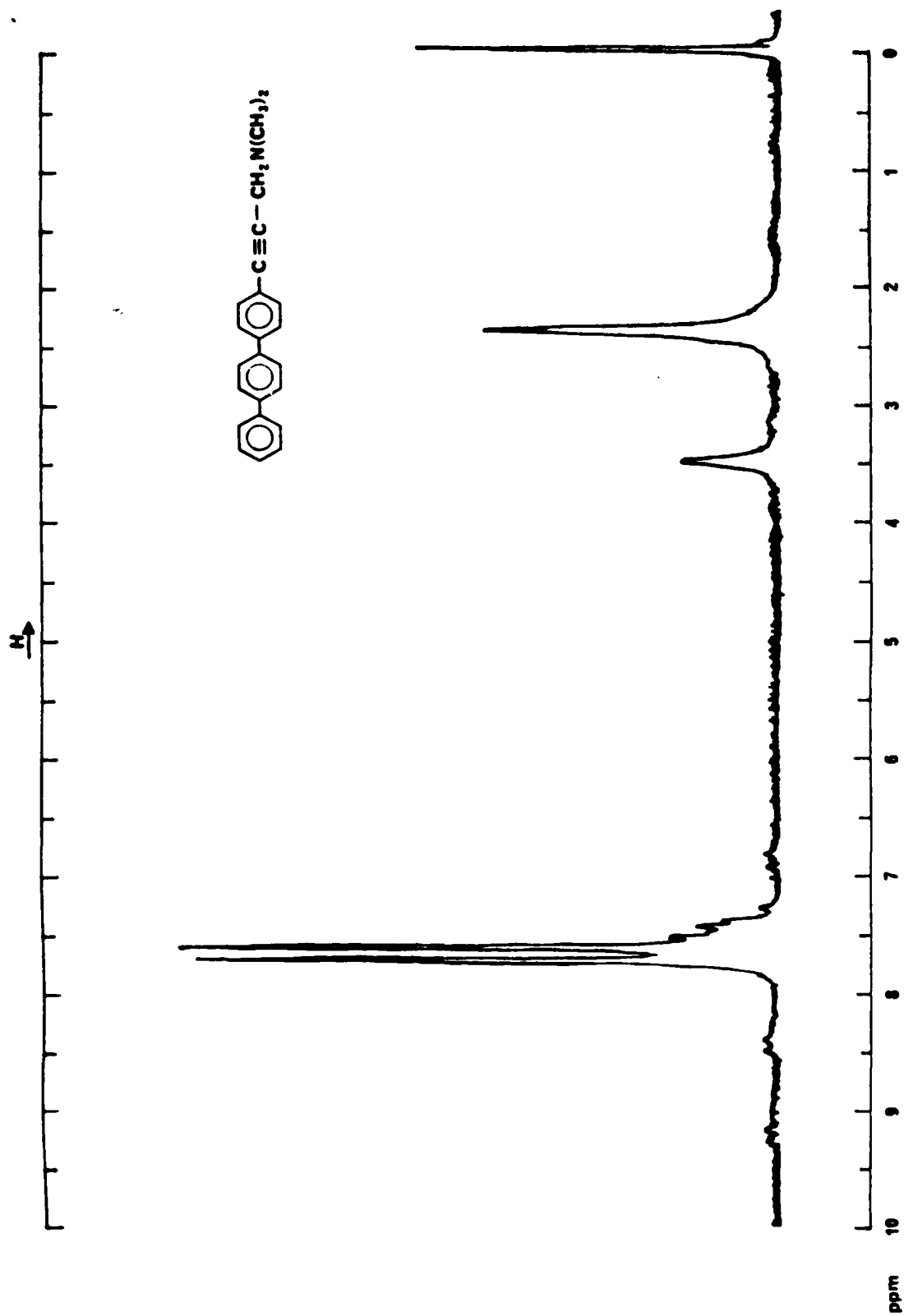


Figure 9. ^1H NMR Spectrum of Monoamine 10d.

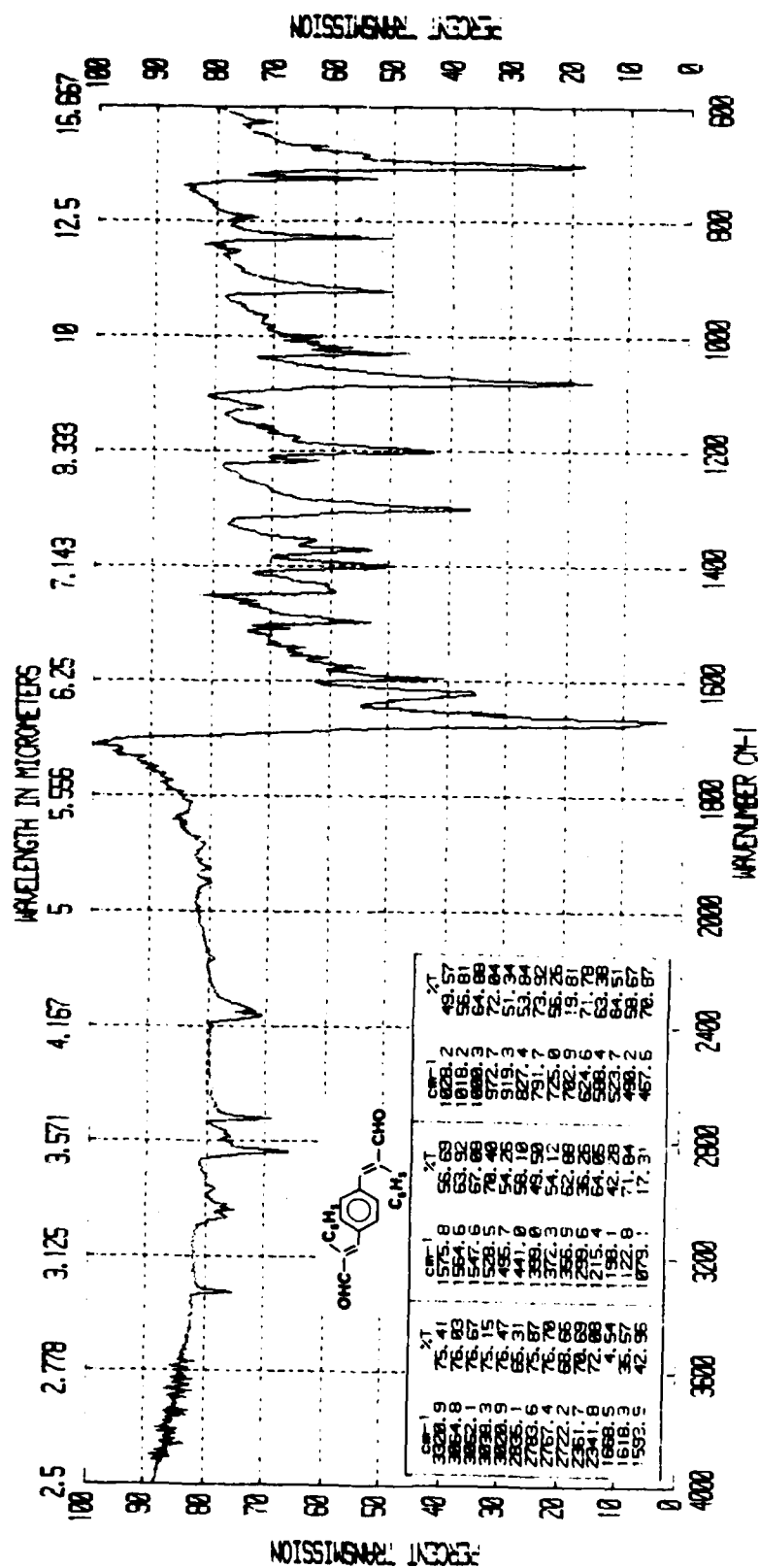


Figure 11. FTIR Spectrum of Compound 6.

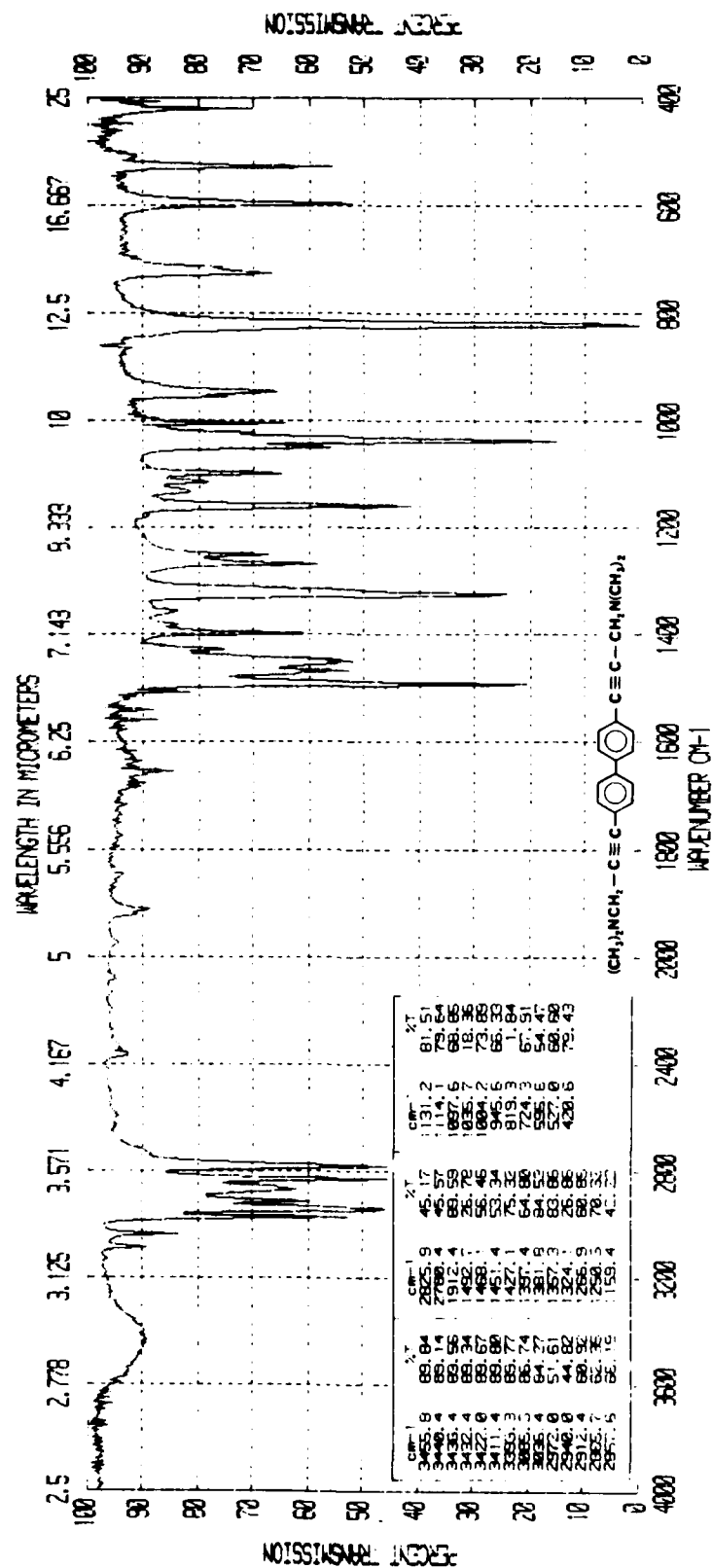


Figure 13. FTIR Spectrum of Bisamine 10b.

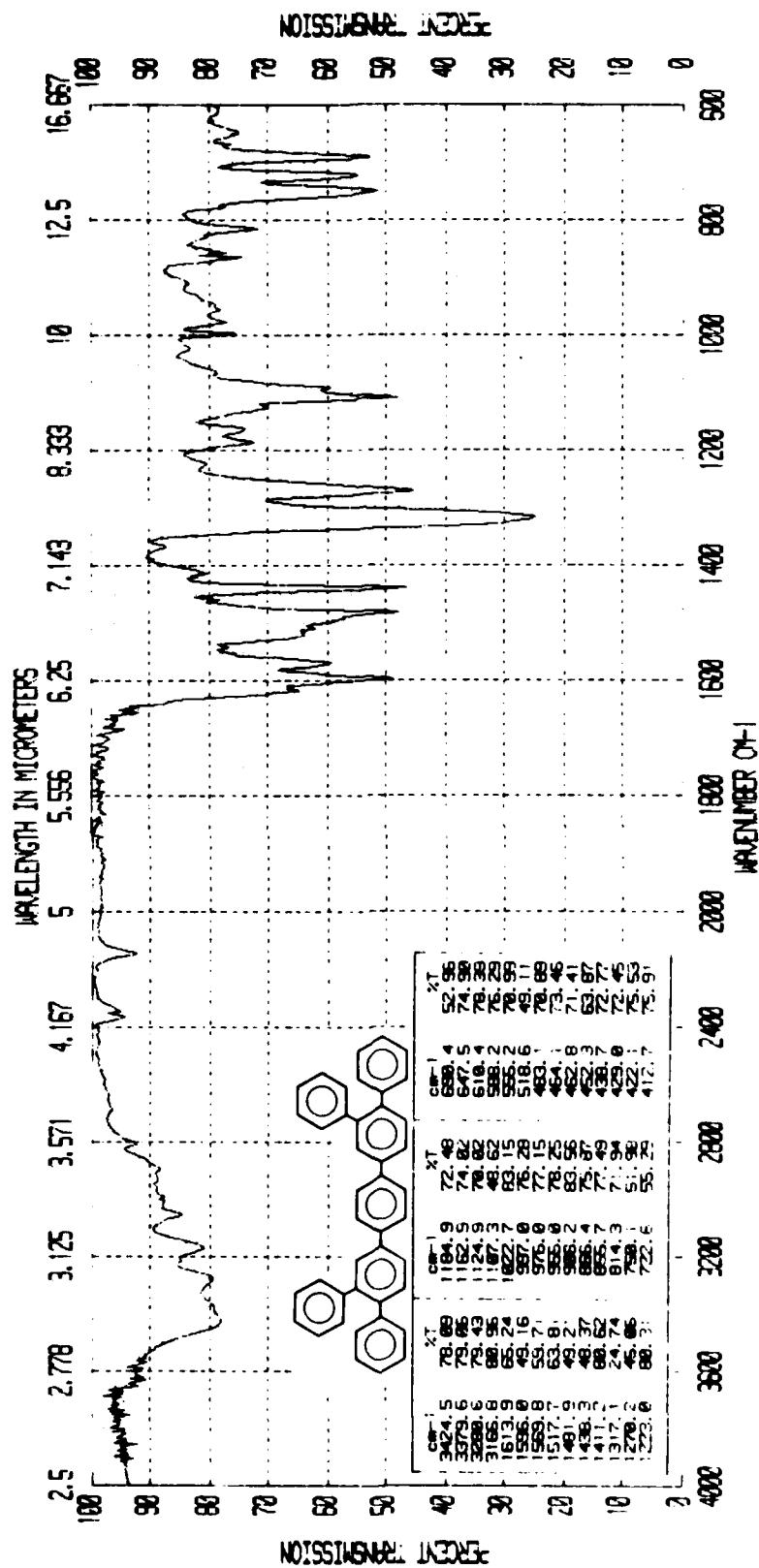


Figure 17. FTIR Spectrum of p-Polyphenyl 15b.

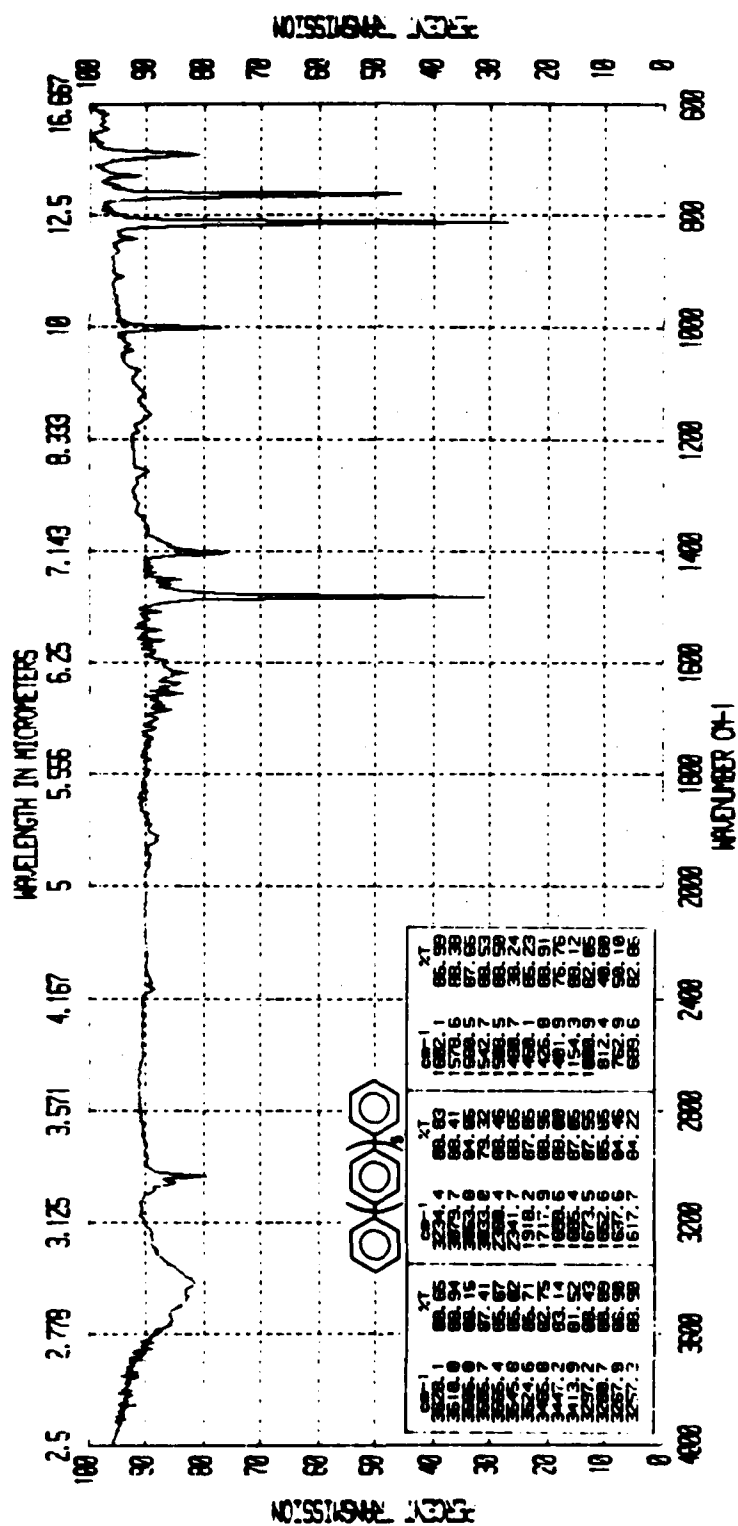
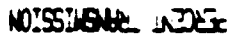


Figure 20. FTIR Spectrum of p-Polyphenyl 15e.



WAVENUMBER CM-1

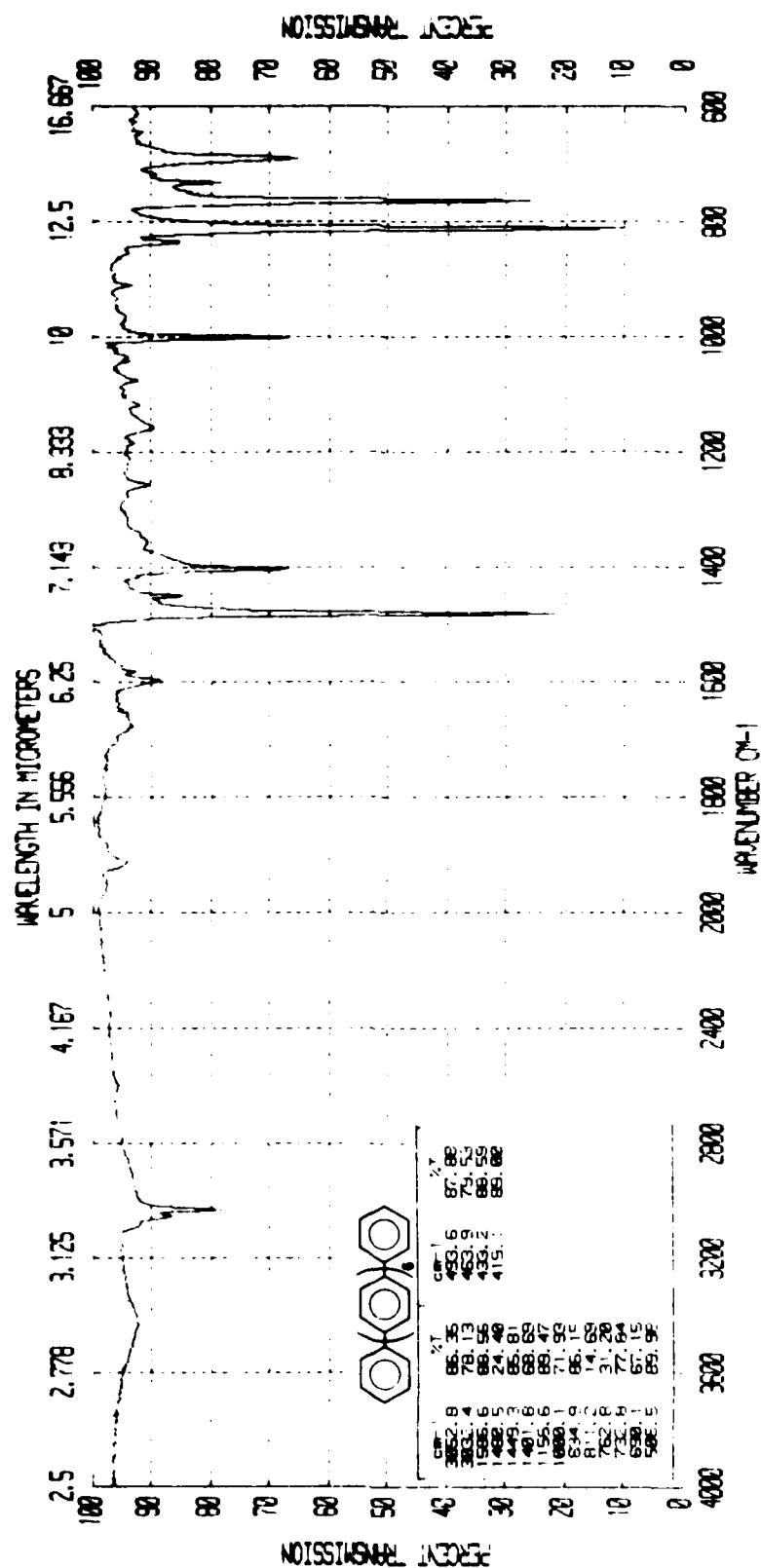


Figure 22. FTIR Spectrum of p-Polyphenyl 15g.

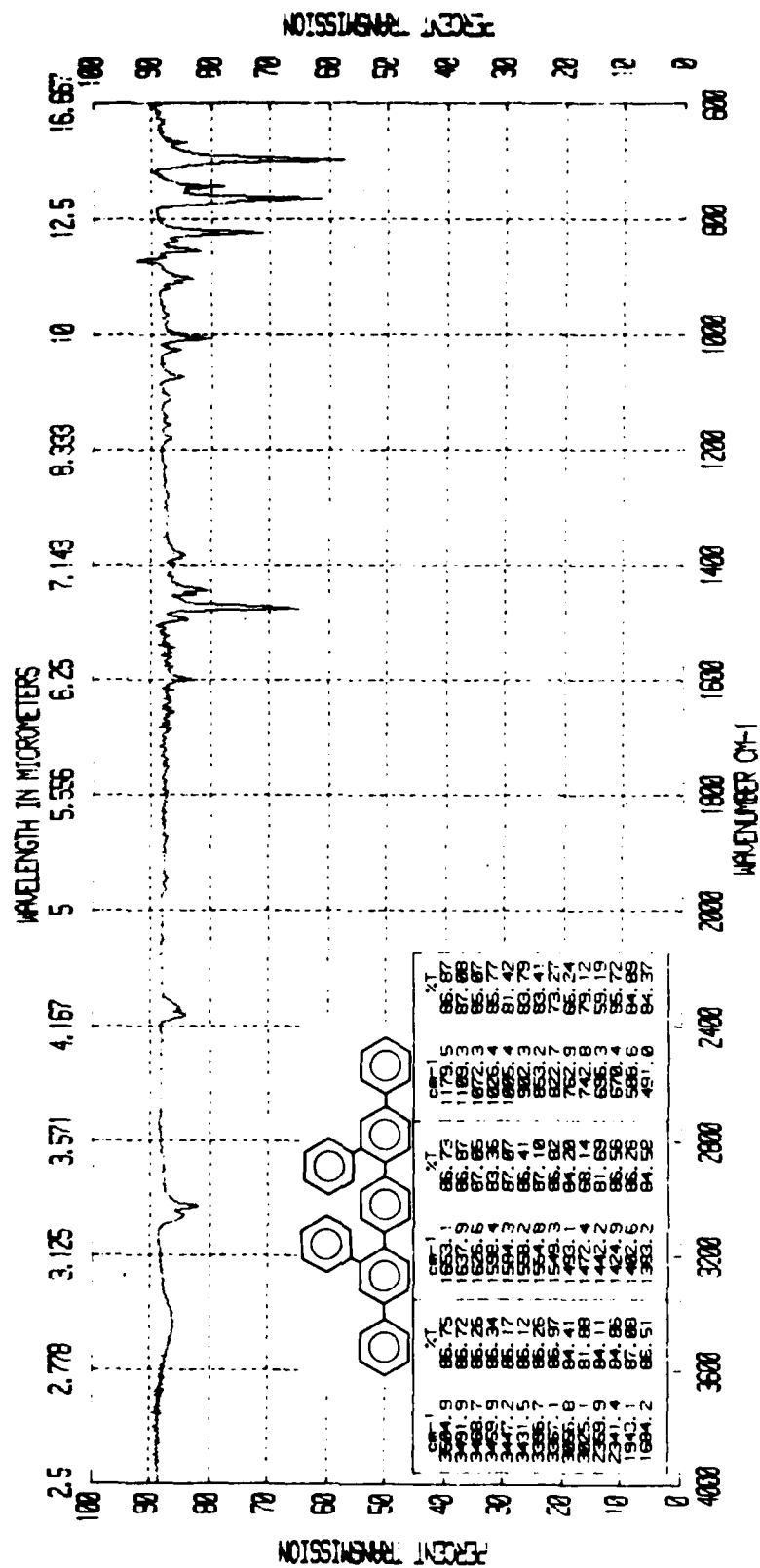
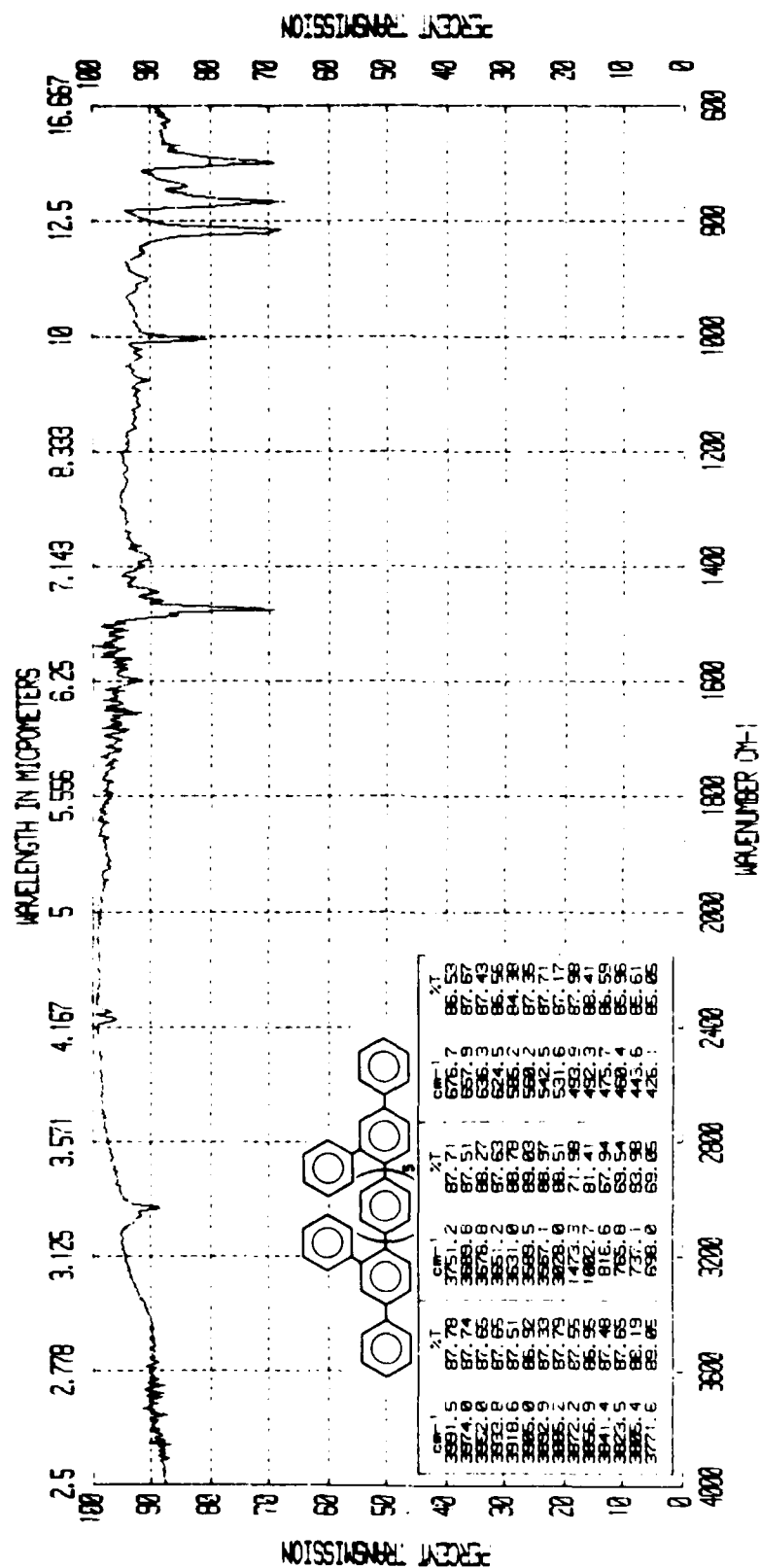


Figure 23. FTIR Spectrum of p-Polyphenyl 21a.



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